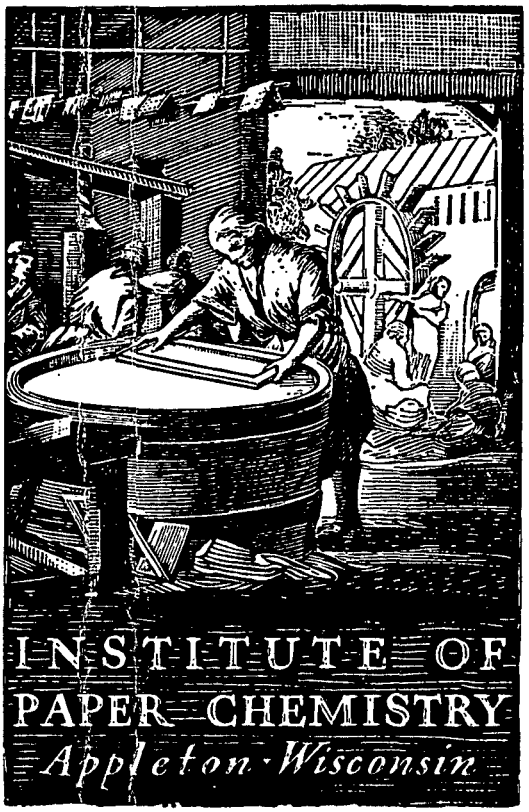

FUNDAMENTALS OF INTERNAL STRENGTH ENHANCEMENT
PART ONE: IMPROVED BONDING VIA CHEMICAL ADDITIVES

Project 3526

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 15, 1984

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

A study has been made of means to enhance the moist and wet strength properties of paper through the use of additives. The additives selected for the program were based primarily on information presented in the literature review which is included in the Introduction of this report. This applies in particular to the work of Espy (22), Zunker (23), and Davidson (24). The mechanism of strength enhancement in the presence of the additives is assumed to include one or more of the following; hydrogen bonding, ionic or electrostatic bonding, and covalent bonding. Several series of tests were conducted utilizing (1) a commercial lightly beaten high alpha pulp and (2) two samples of unbleached southern pine kraft pulp prepared at the Institute.

The high alpha pulp was selected for the first series so as to eliminate the influence of hemicellulose and lignin components. The pulp was not classified, and deionized water was used in forming the handsheets to avoid the effects of water hardness and other multivalent ions. Carboxymethyl cellulose (CMC) was utilized as an anionic additive and polyamide polyamine epichlorohydrin (PAE) was utilized as the cationic component in the first series of tests (22). Combinations of these materials added separately at selected rates produced substantial improvements over blank and PAE controls. Moist tensile factors reach values of 2.6 compared to 1.0 for the PAE controls, and wet tensile factors reach 17.5 compared to 3.1 for the controls. (Note: moist tensile factor is arbitrarily defined as the ratio of the moist tensile strength of the treated

paper to that of the untreated controls. A similar definition applies to wet tensile factor). An optimum CMC/PAE ratio of 0.4 was reported by Espy (22), and this was found to apply at the 2.5% PAE addition level.

Additional series were undertaken employing 47-49% yield unbleached southern pine kraft pulps incorporating CMC/PAE, PVA/TMM (polyvinyl alcohol/ trimethylol melamine) and PVA/PAE combinations in tap water. The pulps were classified prior to use in handsheets in most cases. The PVA/TMM series was pursued on the basis of results reported by Zunker (23), while the PVA/PAE series represents an alternate anionic/cationic combination. In several cases, the PVA/TMM and PVA/PAE combinations were utilized in conjunction with polyacrylic acid (PAA) (24) in an effort to induce covalent bonding through ester formation.

When utilized in the beaten and classified kraft pulp, CMC/PAE combinations again produced significant improvements over the PAE controls, in this case at total additions of 0.7 to 2.1% based on fiber. Moist tensile factor reached 2.6 and wet tensile factors reached 17.0 at a total addition of 1.4% (CMC/PAE - 0.4) compared to 1.83 and 12.77, respectively, for the 1.5% PAE controls. CMC/PAE also provided substantial improvements in dry and moist tensile energy absorption (TEA), stretch, and dry in-plane moduli in most comparisons. Some improvements in extensional stiffness (Et) were also achieved. When CMC/PAE ratio was explored over a range of 0.25 to 1.0 at a total addition of 1% based on fiber, a consistent advantage with respect to ratio was not evident, although improvements over the controls were obtained in most cases. In general, maximum dry tensile properties occurred at ratios of 0.2 or 0.4, but such was not necessarily the case in moist tensile properties. Thus, CMC/PAE ratio did not prove to be critical in the presence of tap water as opposed to deionized water (22).

Additional studies with CMC/PAE combinations revealed that correcting the treated papers to constant density reduced moist and wet tensile factors somewhat but did not alter the conclusion that CMC/PAE produced superior strength properties. Further, little or no difference in moisture content was found between treated and untreated papers when exposed to relative humidities ranging from 50-93% at 73°F. The addition of sizing agent had a relatively minor effect on the strength properties in CMC/PAE-treated papers. It was found that none of the polymer combinations used in the program provided water resistance. The presence of fines in CMC/PAE-treated papers lowered moist and wet tensile factors but this was due, at least in part, to the higher moist and wet strength properties of the untreated controls. In any case, the CMC/PAE-treated paper maintained some advantage over the PAE controls in the presence of fines.

PVA/TMM and PVA/PAE combinations also produced improvements in strength properties. Of the two series, PVA/TMM provided rather consistent advantages over PVA/PAE. However, when combined with polyacrylic acid (PAA), PVA/PAE produced notably higher strength properties and, accordingly, further work with PVA/TMM was abandoned. Addition of 0.3, 0.5, and 1.0% PVA/PAE (1:1 by weight) in combination with 1% of PAA (based on fiber) produced moist and wet tensile factors of 2.3 and 15.0, respectively. At the same time, dry and moist TEA, extensional stiffness, and stretch also increased to levels notably higher than those of the PAE controls.

Based primarily on cost considerations, the decision was made to reduce the PAA level to 0.1% since the 1% level used in the earlier tests had not been established as optimum. It was also decided to substitute other, less costly, polymers for PVA.

The other polymers selected for this purpose were guar gum and cornstarch, which are established strength additives for paper. The results indicated that the primary components in these combinations were PAE and PAA. Guar gum and starch produced modest additional advantages in moist and wet tensile factors, while PVA proved the least effective of the three polymers. Moist and wet tensile factors of 2.6 and 18.0, respectively, were achieved by PAE/PAA alone (0.5% of PAE + 0.1% of PAA based on fiber). These results were accompanied by high levels of TEA, extensional stiffness, stretch and Young's modulus when compared to the PAE controls.

The foregoing results provided a basis for the final series of tests with the 47-49% yield pulp. These tests examined the effects on strength properties of PAA/PAE ratio over a range from 0.1-1.0 and PAA molecular weight at values of 5,100, 104,000 and 300,000-500,000. The results revealed that the amount of PAA used in conjunction with 0.5% of PAE had a relatively minor or inconsistent effect on strength properties. In general, breaking length, TEA, and stretch reached maximum at PAA/PAE ratios of 0.1 to 0.4, while dry Et reached maximum at a ratio of 1.0. Strength properties showed a slight dependency on molecular weight, but with little or no advantage beyond a molecular weight of 104,000.

Considerable time was spent in the chemical analysis of treated papers to determine the mechanism by which the multicomponent systems produced superior strength properties. In effect, the goal of this part of the program was to determine if ionic and/or covalently bonded structures were involved. Treated papers and noncellulosic controls were subjected to electron spectroscopy for chemical analysis (ESCA), to GLC/mass spectroscopy, and to Fourier Transform

Infrared analysis (FTIR). In the latter case both transmittance and reflectance methods were employed, including multiple internal reflectance (MIR). Of these, FTIR analysis using diffuse reflectance on samples of Whatman filter paper and glass fiber filters treated with PAE, PAE/CMC and PAE/PAA provided the best information. The results indicate that ester formation and, therefore, covalent bonding occurs between PAE and CMC and between PAE and PAA in the absence of cellulose. The results further suggest that a higher level of ester formation occurs when these components are applied to cellulose. Thus, some covalent bonding between the polymers themselves and between cellulose and the polymers was indicated. This, of course, does not exclude other forms of bonding including hydrogen, ionic, or other covalent bonds. Nonetheless, this information provides the only explanation available at this time for the high levels of moist and wet strength provided by the multicomponent systems. Possible configurations for covalently bonded structures are included in the "Discussion of Results".

Finally, in supplementary tests, means to repulp paper containing PAE/CMC and PAE/PAA were examined briefly. In general, the results indicate that these papers can be repulped in approximately the same manner as those containing PAE alone. A comparison was made of repulping at pH 11 and 66°C against pH 7 and 50°C with 2% of hypochlorite. Repulping at the higher pH and 66°C provided the better results based on the Thwing formation values of handsheets formed from the repulped stock. The Thwing values approached but did not quite equal that of the control. Hence, slightly longer or more intensive repulping may be required.

INTRODUCTION

This is Progress Report One on Project 3526 entitled, "Fundamentals of Internal Strength Enhancement". This phase of the program is concerned with improved bonding via chemical additives. More specifically, means to improve moist and wet tensile properties are of particular interest.

Before laboratory work was initiated, a literature review was prepared directed to mechanisms of interfiber bonding. The review is included here as part of the present report.

MECHANISMS OF INTERFIBER BONDING - A LITERATURE REVIEW

The following review covers modes or mechanisms of interfiber bonding with particular emphasis on research completed since 1969. It should be borne in mind that the preponderance of literature prior to that time was concerned with hydrogen bonding, and this subject must be included in any comprehensive review of interfiber bonding.

The various modes by which fiber-to-fiber bonds may be formed has been described by Allan and Laine (1). These authors approach bonding in nonwovens on the basis of the energy involved. They start at the lowest energy level with binders dependent on Van der Waals' forces with an enthalpy of ~1-2 kcal/mol; and continue through hydrogen bonding at 3-8 kcal/mol, ionic bonding at 10-13 kcal/mol, and finally covalent bonds at 70-100 kcal/mol. In the case of rayon (cellulosic fiber) Van der Waals' forces readily equate to hydrogen bonding. This mode of interaction is particularly suitable for cellulosic webs because aggregates of the cellulose molecules are themselves held together by hydrogen bonding, and in paper, these are said to be responsible for the cohesion of the sheet.

The role of Van der Waals' forces and the formation of hydrogen bonds in paper has been reviewed by Swanson (2). It is well known that a wet sheet made from highly swollen fibers is still weak after extensive pressing. Therefore, there are few permanent bonds formed in the conventional pressing operation. However, during the drying operation, a mechanism known as the "Campbell" effect brings fibers into sufficiently intimate contact to form hydrogen bonds. When the fiber content of the web on the forming wire is about 8%, the web is held together by surface tension forces arising from the meniscus formed as the water layer recedes into the fibrous structure. As long as the radius of curvature of the meniscus is sufficiently large, the principal force, F, pulling the fibers together is approximately $F = \gamma L$ where γ is the surface tension in dynes/cm and L is the length of the line contact between air, water, and fiber.

As the water recedes further, a second stage develops in which two menisci exist between adjoining fibers when the compacting force will be approximated by $F = 2\gamma L$. The compacting pressure at this point has been estimated to range from approximately 0.6 to 6.0 psi depending upon fiber and fibril size and spacing. While this pressure is appreciable, it is not sufficient to produce appreciable wet web strength. At about 20-25% solids, a transition stage is encountered where, due to compacting pressure, sheet density increases and interfiber bonding begins to occur. In this region the total surface tension forces decrease very rapidly and the water content of the sheet becomes so low that the liquid water film becomes discontinuous. However, the magnitude of the pressure difference caused by the surface tension forces changes from a dependence upon the total length of the fiber-water-air contact to a dependence upon the thickness of the water film held between two fibers nearly in contact. The latter effect may be expressed approximately by $\Delta P = \frac{2\gamma}{x}$ where x is the

thickness of the water film and ΔP is the compacting pressure. This pressure reaches values on the order of 100-200 atmospheres as the sheet approaches dryness. This then is the major effect which is responsible for the final compacting pressure that forces the plasticized fibers sufficiently close together for hydrogen bonds to form. Evidence supporting this bonding mechanism may be found in the fact that cellulose fiber webs exhibit little strength if the water is replaced by a nonpolar solvent in the forming operation or if the water is removed by freeze drying.

Page, Tydeman, and Hunt (3) indicate that hydrogen bonds must play a large part in providing paper strength, but they do not claim that hydrogen bonds are solely responsible. These investigators studied fiber-to-fiber bonding directly, using a light microscope at medium power and vertical illumination. The contrast in the image by this simple method is normally too low, but by incorporating dyed fibers within the sheet and by using polarized illumination with a crossed analyzer, the contrast was enhanced to a useful level. The technique revealed regions of optical contact between two adjacent fibers. The authors list two possible mechanisms by which areas of optical contact may form: (1) by collapse of one fiber on another due to the large forces of wet pressing and surface tension, and (2) by accumulation at the regions of crossing (owing to surface tension) of residual water which upon drying will deposit its dissolved and suspended material. Even in the case of simple bonds (one fiber crossing another), all of the common area of crossing is not usually bonded; rather, a whole range in degree of bonding exists. It was considered likely that beating affects the local plasticity of fibers sufficiently to allow individual areas of contact to merge together, increasing the degree of bonding at a crossing.

The variables available to the papermaker wishing to change the physical properties of the sheet consist mainly of fiber furnish, beating, pressing and drying conditions. There is an overriding effect of furnish on the absolute bond size, since fiber width is a controlling factor. Therefore, fiber surface topography and fiber plasticity in different furnishes will have a major effect. It was shown that beating increases the bond size of a softwood furnish, and it is expected that wet pressing would have a similar effect. On the other hand, drying tension, which has a major effect on the physical properties of the sheet, appears to have only a small effect on bond size and, if anything, tends to reduce it. The absolute values of the interbond distances are also highly sensitive to fiber furnish, being dependent not only on fiber width but also on fiber flexibility. Beating decreases the distance between bonds and the action of wet pressing might be expected to give a similar result. The speculation was made that the combined effect of bond size and the distance between them could control many of the physical properties of paper.

James d'A. Clark (4), in treating the matter of hydrogen bonding, indicates that only about 10-20% of the area of fibers appearing to be in optical contact is actually in sufficiently close contact for hydrogen bonding to occur. Further, some of these areas are not completely bonded, since it has been estimated that only 0.5 to 2% of all the hydroxyl groups present on the interfiber surface of paper are involved in bonding. Clark mentions chemical modification which may be accomplished by partial substitution of, or addition to, the available hydroxyl groups, especially by hydroxyethylation which almost doubles their bonding ability. It is surmised by Clark that the linkages between adjacent cellulose molecular chains are provided mainly by the primary OH groups because they extend farther from the chain and have greater mobility and

reactivity. Thus, if a sufficiently attractive group is available other than the adjacent OH group on the other chain to which it is hydrogen bonded, this primary OH group will combine with the new group and so detach itself from the hydroxyl group on the adjacent chain. The remainder of the entire cellulose structure is thus loosened and made more accessible to water, more flexible, and more easily fibrillated. All these provide greater fiber-to-fiber cohesion, provided the substitution is minimal.

Clark also briefly discusses ionic or electrostatic bonding wherein a cationizing chemical (polyethylenimine) was sprayed as a mist onto wet, newly-formed sheets. When sufficient chemical was applied to reverse about 10% of the negative charges, an increase of about 50% in dry tensile strength was achieved. In contrast to hydroxyethylation, which decreased wet tensile strength, a ten-fold increase in wet strength was attained.

The use of ionic bonds in the development of paper strength has been described by Allan and coworkers (5,6). The relatively small improvement in tensile strength normally obtained when cationic macromolecules are added to naturally occurring anionic pulp is ascribed to the small number of ionized sites on the fiber surface. The energy of ionic bonding is then small in relation to the total energy of the hydrogen bonds. Introduction of a large number of anionic sites was accomplished by treating the pulp with a fiber reactive dye containing two sulfonic acid groups. Neutralization of these anionic sites by spraying onto the surface of the web a series of polyamines produced significantly stronger paper when the molecular size of the polyamine was greater than 15Å. The zero span tensile strength was also increased by the larger amines. This increase in intrinsic fiber strength is attributed to a reduction in the

adverse effects of the large discontinuities in the lamellar cell wall. In contrast, stable wet strength was induced by ionic bonding generated by both large and small polyamines because even the limited bond energies of ionic bonds (10-13 kcal/mol) is large in comparison to the total energy of hydrogen bonding in wet paper. Bonding based on electrostatic or ionic linkages is said to have the following advantages:

1. Ionic bonds are formed instantaneously in aqueous media and need no subsequent curing period.
2. Compounds capable of forming ionic interfiber bonds are often soluble in water.
3. Ionic bond formation is reversible, i.e., if such linkages are ruptured, bond formation requires only realignment of the formerly charged atoms.
4. Electrostatic attractions can occur over greater intermolecular distances than those required for covalent bonding.
5. Cellulose or lignocellulosic fibers are very amenable to ionic reactions because of their natural anionic character.

In investigating the effect of ionic bonding on the wet strength of paper, a series of polyamines was sprayed in increasing amounts onto both dyed and undyed handsheets, so that the desirable balance of positive and negative sites would be achieved. The results revealed that the polyamine-treated, but undyed, papers possessed much lower wet strength than their dyed counterparts. It was concluded on the basis of these results that ionic bonding is an effective means of producing water resistant bonds (>40% wet strength). The validity of this view is supported by the long-term durability of the wet strength. Dyed

handsheets treated with pentaethylenehexamine retained their original wet strength through continuous immersion in water for 30 days. The considerable wet strength developed with the lower molecular weight amines cannot reasonably be attributed to the formation of a protective sheath around preexisting bonds, which is commonly assumed to be the mechanism by which conventional wet strength resins operate. It should be pointed out that when higher molecular weight polyamines were added to a sheet mold containing the dyed fibers, gross flocculation occurred. Hence, the spray application of the polyamines was adopted.

Interfiber bonding based on electrostatic forces is the subject of a number of papers by Frolov (7-9). Frolov claims that phenomena exist both in theory and in papermaking practice which cannot be satisfactorily explained on the basis of hydrogen bond theory. According to his theory, the formation of charges on the surface of fibers or their structural elements is the result of donor-acceptor interaction of dipole water molecules with polar groups of cellulose. Unlike the short-range forces characteristic of hydrogen bonds, the electrostatic forces, because of a "micromosaic" distribution of charges on the fiber surface, have a long-range (ionic) character. In support of his approach to bonding, he points out that a substantial increase in bonding strength (20-30%) occurs at the isoelectric point when the zeta potential is zero. He further claims that paper strength is related to the dielectric constant in accordance with the equation $P = B \cdot \frac{1}{\varepsilon}$ where P is paper strength in a medium having dielectric constant ε, and B is an empirical coefficient characterizing the share of electrostatic forces in the overall bonding strength. Thus, the inversely proportional dependence of paper strength on the dielectric constant of the medium is taken as confirmation of the important role of the electrostatic component in the mechanism of interfiber bond strength. The share of the

electrostatic forces in the overall strength of the bonds is indicated to be at least 30-35% in the dry state.

Placing paper with "ruptured" bonds in a nonpolar medium and the medium evaporated (conditions under which hydrogen bonds cannot be formed) resulted in the regeneration of 45-60% of the initial strength. This was taken as further confirmation of the important role of electrostatic forces in the mechanism of interfiber bonding. Frolov also detected emission of electrons during degradation of paper in vacuum. This was considered confirmation of the presence of interfiber contact zones of high-intensity electric fields.

Frolov concludes that interfiber bonding in paper is a more complex phenomenon than previously assumed. There are good reasons to assume that, in paper, in equilibrium moisture content with its surroundings, the bonds between fibers are formed mainly by the mechanism: cellulose-aqueous layer-cellulose under the action of an intense electrostatic field in the double electric layer formed as a result of donor-acceptor interaction of water molecules with the functional groups of cellulose fibers.

In the third paper in the series (9), Frolov considers practical means of improving paper strength properties by regulating the parameters of the electric double layer. He recognizes that the combination of hydroxyl and carboxyl groups in natural cellulose is not the best from the standpoint of their donor-acceptor properties. He lists the following functional groups in the order of their decreasing donor (increasing acceptor) properties: -NH>-OH>-OCOR>-C_6H_5>-Cl>-COOH>-CN>-C=C-(Rubber). An increase in interfiber bonding was achieved through a fixation of donor groups on the surfaces of one part of a cellulose fiber furnish and acceptor groups on another part. Paper was then

formed from a 1:1 mixture of the positively and negatively charged fibers. In one case cyanuryl cellulose (CC) was used as the negatively charged component and aminoethyl cellulose as the positively charged component. While chemically modified cellulose can be used to increase interfiber bonding, a more practical approach would consist in the adsorptive modification of cellulose. In pursuing the latter approach, cationic fibers were produced by treating 1% consistency pulp with an aqueous solution of polyethylenepolyamine. Anionic fibers consisted of untreated cellulose and fiber treated with carboxylated acrylonitrile latex. The results indicated that a 1:1 mixture of these fibers produced higher strength than that produced from either component alone. It becomes expedient in the case of both chemical modification and adsorptive treatment to select donor and acceptor groups which will react together and with cellulose so as to form water resistant bonds. For example, it was stated possible to achieve 100% wet strength when using epoxy cellulose as a stock additive.

The effect of chemical interfiber bonds on the wet strength of paper was examined in an earlier paper by Dobysh and Frolov (10). Dobysh and Frolov cite Allan's work with ionic bonding but comment that the model developed by Allan does not exclude other mechanisms of wet strength development and does not give clear qualitative evidence of chemical bonds or a quantitative evaluation of their effect on the wet strength of paper. In attacking the problem, paper was made from a mixture of two types of cellulose containing functional groups capable of reacting with each other during the process of drying. It was reasoned that, as a result of interfiber condensation, part of the hydrogen bonds should be replaced by chemical bonds. The topological character of the model presupposed the formation of only chemical bonds between the fibers, considering that distance between structural elements is small and sufficient for

the formation of such bonds. In pursuing this approach, aminoethyl cellulose (AEC) and monocarboxyl cellulose (MCC) were synthesized as the two components for one series of tests. Paper prepared from a 1:1 mixture of AEC and MCC had a strength which was 20 and 100% higher than papers prepared from AEC or MCC, respectively. Spectral analysis of the paper confirmed the possibility of interfiber cross-linking of cellulose in paper by the reaction of reactive groups at the points of their contact. However, the model gave only a qualitative characteristic of the effect of interfiber chemical bonds on the wet strength of paper. Accordingly, a quantitative evaluation was undertaken using AEC and cyanuryl cellulose. The number of interfiber chemical bonds was found to increase with increasingly active surface of the cellulose fiber, although in this case increasing the degree of substitution resulted in sheet formation difficulties owing to the poor wettability of the cyanuryl cellulose component.

In practice, a two component system involving modified cellulose fibers would probably be used only when high wet strength is required as exemplified by the use of modified cellulose containing an epoxy group reactive with cellulose hydroxyls. The wet strength of such paper is stable and does not depend on the time of immersion in water.

In a subsequent paper, Frolov and Dobysh (11) reaffirm the donor-acceptor (DA) mechanism of bond formation and indicate that the formation of hydrogen "bridges" at the point of fiber contact is an extreme case which is not fully achieved in conventional papers due to the high rigidity of the cellulose macromolecules. Because of the specific character of the DA interactions due to the transfer of electric charges from the donor to the acceptor, the electrostatic component contributes to a considerable extent the overall energy of the bonds. At the same time the authors concede that hydrogen bonds, with

participation of water molecules, can be formed between the fibers. Thus both theoretical considerations and experimental data confirm the possibility of reaction between fibers or microfibrils at their point of contact in air-dried paper through the hydration layer having the thickness of a few water molecules. The authors describe a method for measuring the thickness of the hydration layer using bifunctional compounds of known molecular weight and length. The assumption is made that in paper varying in moisture content, water resistant bonds can be formed only under the condition that the thickness of the hydration layer at the fiber contact point is smaller than or equal to the length of the cross-linking agent molecule. It would be expected on this basis that the longer the molecule, the higher the moisture content of the paper and the corresponding thickness of the hydration layer at which the wet strength of paper increases significantly. In support of this theory, the authors used formaldehyde (av. length 9.06Å) and dimethylol urea (19.9Å) as the cross-linking agents and found that the bulk of the wet strength bonds with formaldehyde occurred at a moisture content of 7.5%, whereas, in the case of dimethylol urea, the optimum shifted to ~16.2% moisture content. Most of the fibers in contact in air-dried paper are separated by a hydration layer 8-10Å in thickness. Information of this nature should be of great importance to papers and cartons which are stored and/or used under high humidity (jungle) conditions.

Frolov, Umanski, and Dobysh (12) consider three methods for imparting wet strength to paper through the formation of chemical interfiber bonds, i.e.,

1. Use a two component system of modified cellulose fibers containing functional groups capable of reacting with each other but inert with respect to cellulose hydroxyls;
2. Use as a wet strength additive, modified cellulose fibers containing functional groups which react with cellulose hydroxyls;

3. Treat paper made from usual or modified cellulose with bifunctional compounds in order to cross-link the fibers in the web.

These methods were treated on a theoretical basis starting with the last approach. The probability of forming chemical interfiber bonds under ideal conditions was calculated. It was concluded that the first method would have limited possibilities of imparting wet strength to paper, but the second method involving, for example, the use of modified cellulose containing reactive epoxy groups was indicated to have considerably greater potential for improving both dry and wet strength.

The concept of multicentered hydrogen bonding is described by Akagane, Allan, et al. (13). The specific shortcomings of typical water soluble vinyl polymers as adhesives for cellulose are outlined, and the DNA-inspired concept of multicenter hydrogen bonding is presented as a means of producing enhanced fiber-polymer interactions. In order to achieve bonding improvement within the area of fiber crossings, two distinct approaches are visualized:

1. the number of interfiber hydrogen bonds could be increased, or
2. the number of bonds could be held constant but their intrinsic energy could be augmented.

The first approach is most frequently accomplished by beating or refining. The second approach is only beginning to receive significant attention at the higher end of the bond energy scale, i.e., ionic (electrostatic) and covalent bonding. In pursuing the second approach, it must be borne in mind that cellulose in pulp and paper will always be associated with water molecules which occupy potential hydrogen bonding sites. The formation of new hydrogen bonds to the cellulose

macromolecules will require displacement of this combined water with more stable ligands. It was proposed to synthesize ligands capable of exactly mating with the stereochemical surfaces of the cellulose so more ordered interactions of higher enthalpy are thereby achieved. This type of precise hydrogen bond mating is exemplified in nature by the bonding of the two strands of the double helix of the DNA molecules where the purine, adenine, and thymine combine only with pyrimidines, guanines, and cytosine, respectively. The result is a di- or tri-centered hydrogen bond linkage representing bond energies significantly greater than the hydrogen bond energy in paper.

The multiple cohesive linkages of the strands of the DNA double helix were simulated by the interactions of the hydroxy group of cellulose with the imidazolic acrylate analogs of the purine-pyrimidine pairs. Among the imidazolic monomers, [acryloxy-2(pyrid-2-yl)-4,5 dimethyl] imidazole (APDMI) had the best combination of cellulose substantivity and ease of synthesis. Adhesive comparisons of a representative copolymer of APDMI-acrylamide with polyacrylamide in webs of regular and markedly anionic rayon fibers were used to show that ionic bonding does not contribute to the significant enhancement in tensile strength produced by the presence of multicentered hydrogen bonding sites in small amounts. The results tend to confirm that multiligand hydrogen bonds can play an effective role in bonding cellulose fibers without chemical premodification of the cellulose fiber surfaces.

Haddad (14) proposes a theoretical, atomistic approach for the bonding between fibers on the basis of unit cell theory and the assumption of corresponding matching points analogous to the theory of coincident site lattices. An actual bonded area within the junction is defined and related to the effective

number of bonds acting between two fibers. The response behavior of the bonding is formulated by using a bonding potential form which is valid within the actual bonded area. A possible bond breakage in the junction, i.e., when the bonding deformation exceeds its maximum limit, was treated as a stochastic process which was assumed to follow a stationary Markov chain.

Neogi and Jensen (15) describe wet strength improvement by means of surface modification through ionic and covalent bonding. Ionic bonding was achieved by the use of charged fibers, followed by treatment with an oppositely charged polyelectrolyte, for example, CMC fibers and polyethylenimine. Covalent bonding was achieved by oxidation of fiber surfaces to generate reactive aldehyde groups followed by cross-linking with polyamine in nonwoven webs. Alternate means to achieve covalent bonding was via heat treatment only and heat treatment coupled with cross-linking. Wet strength levels up to 52% were achieved with covalent bonds.

Additional references concerned with interfiber bonding, wet strength, and/or means to measure interfiber bonding are presented in the following section.

A patent by Stofko and Zavarin (16) describes a method for improving interfiber bonding among fibers from high lignin content pulps like groundwood, semimechanical, and semichemical. Improved bonding is achieved by thoroughly dispersing throughout the pulp an oxidizing agent which results in the formation of interfiber chemical linkages effected by oxidation upon the application of heat. The patent indicates that an oxidizing agent such as hydrogen peroxide can be sprayed or coated onto the paper web along with a catalyst such as zirconium tetrachloride or ferrous sulfate.

Horn (17), in addressing bonding in press-dried sheets from high yield pulps, proposes that the hemicelluloses are primarily responsible for the high strength properties associated with press-dried pulps. It is further proposed that the improved compression creep properties of press-dried pulps result from lignin flow which protect pre-existing bonds against moisture penetration.

It is hypothesized that as the temperature in the sheet increases, the hemicelluloses, owing to their lower softening temperature, are readily plasticized and begin to flow. It is important to reach the peak temperature rapidly, since this allows the interaction of the water and hemicellulose to take place over a longer period of time. The benefits of this are said to be twofold: (1) more of the available surface hemicellulose can be utilized by greater flow, and (2) there would result an increased softening effect on the inner constituents of the cell wall, which would promote greater fiber flexibility to create a larger bonded area and the required intimacy between fibers to take advantage of the hemicellulose flow.

Lignin, having a much higher thermal softening temperature, does not have sufficient time to flow like the hemicelluloses (under the temperature range used by this investigator). Even if mass lignin flow occurred, it is doubtful that the strong bonding associated with press drying could be attributed to lignin bonding. It was concluded that lignin bonding does not contribute to sheet strength properties, but it does appear to protect bonds against changing moisture content. In effect, high-yield, press-dried sheets were shown to have compressive creep properties superior to those of conventional sheets made from the same pulp.

Zhukov and Butko (18) subjected unbleached kraft and bleached sulfite pulp suspensions to a magnetic field (223 x 10^3A/m) and found that bonding strength improved 11-16%, depending upon the freeness of the pulp. It was concluded from this work that subjection of pulp to a magnetic field caused a reorientation of the fibers which led to an increase in the number of hydrogen bonds, since there resulted a closer interaction between cellulose molecules, preventing the shift of one molecule with respect to another.

Law, Kokta, and Garceau (19) suggest that measurement of apparent specific heat gives an indication of the internal structure of pulp fibers. High freeness pulps show lower values for apparent specific heat, high tear factor, lower breaking length and burst factor than low freeness pulps. In other words, high specific heat is associated with better interfiber bonding.

Chatterjee (20) describes static and dynamic thermoacoustical techniques for characterizing cellulose fibers. More specifically, three individual topics of the acoustical techniques are briefly discussed, i.e., characterization of interfiber bonding in cellulose sheets, water absorption in a paperlike nonwoven structure, and dynamic thermal analysis of textile fibers including cotton, rayon and varieties of synthetic fibers. The mechanism of sonic pulse propagation in cellulosic sheets at isothermal conditions and in cotton, rayon, and synthetic fibers under dynamic heating conditions are reviewed. The velocity of sonic pulse in a dry cellulose sheet is controlled by the proportion, modulus, and density of two structural constituents of the sheet: the bonded and unbonded fiber regions. This technique was shown to be an excellent nondestructive method for estimating interfiber bonding in cellulose sheets. The technique was also found to have a unique application for studying liquid wicking in cellulose sheets.

Theory and application of dynamic thermoacoustical analysis are described. The method consists of a continuous measurement of the propagation time of sonic pulses through the sample held under light tension and heated at programmed temperatures. The viscoelastic properties of a variety of synthetic and cellulosic fibers were examined by this technique.

Smith and Graminski (21) claim that if the fiber network consists of a relatively small number of fibers (2.5 g/m^2) such that the area covered by more than two fibers intersecting at a given point is negligible, then the forces generated when a specimen is elongated will be significantly lower than necessary to break fibers in the specimen. When the elongation is performed in a sensitive tensile tester, the force-elongation curve consists of jagged peaks. Each peak represents breaking of a bond between two fibers. Integration under the curve produces values for a second curve in which the cumulative work done on the specimen is plotted against the number of bond breaks that may have occurred. Segments of this curve, usually occurring near the end, have minimum slopes. The value of these slopes is equal to the average energy dissipated per bond break by a few fibers near the site of the break and can be considered a measure of bond strength.

Recent publications by Espy (22) and Zunker (23) covering multi-component additive systems (CMC/PAE and PVA/TMM) are of particular interest to this program as is a patent by Davidson (24).

EXPERIMENTAL

HANDSHEET STUDIES - ALPHA CELLULOSE

A series of exploratory tests was conducted in an effort to establish the potential of ionic (electrostatic) or covalent bonding as a means to enhance the dry, moist and wet strength of fibrous webs. For this purpose, a high purity pulp, i.e., a 97% alpha cellulose, was selected so as to essentially eliminate the possible influence of hemicellulose and lignin residues on the interaction of the components to be added. This is normally a weak pulp which is difficult to improve in strength properties. Accordingly, unusually high additive levels were employed. The alpha pulp was beaten to a freeness of 415 mL CSF and then dewatered to approximately 30% solids and stored at 40°F without preservative. The fines content was 15%. Sufficient pulp to prepare a set of handsheets was redispersed in deionized water at 1% consistency by subjecting the suspension to 300 counts in a British Disintegrator. The fiber slurry was then diluted with deionized water to provide a consistency of 0.5% for subsequent sheetmaking. Each additive was metered as a 1% aqueous solution into the pulp followed by five minutes of stirring. A measured amount of fiber, sufficient to form a 2.5 g handsheet, was added to a Nobel & Wood sheet mold along with additional deionized water so as to provide a forming consistency of 0.04%. The forming wire was 100 mesh monel in all cases. The handsheets were couched from the wire onto blotter stock, followed by five minutes of pressing at 50 psi and seven minutes drying on a steam drum at 230-235°F. Handsheets from other pulps were prepared in the manner described above. Initially handsheet testing was limited to basis weight, density, dry breaking length, wet breaking length (24 h soak) and sizing. Moist breaking length (16% moisture at 93% RH and 73°F) was determined on a limited basis. Moist tensile factor is arbitrarily defined as the

ratio of the moist breaking length of the treated paper/that of the untreated paper. A similar definition applies to wet tensile factor. NOTE: The average dry weight for each set of handsheets was used in determining dry, moist, and wet breaking length.

On the basis of recent work by Espy (22) handsheets were prepared from the high alpha pulp incorporating polyamide polyamine epichlorohydrin (PAE) and low viscosity carboxymethyl cellulose (CMC; DS 0.7). In this series of tests, the amount of PAE added was 1.0, 2.5, and 5.0% based on fiber, while CMC was added at 0.4, 1.0, and 2.0% at each of the indicated PAE additions. Hence, in each subseries, a set was included in which the CMC/PAE ratio was 0.4. This is the ratio which Espy had established as being optimum or near optimum for demineralized water systems using CMC of DS = 0.7. Results are recorded in Table 1. Strength properties as a function CMC/PAE ratio are presented in Fig. 1-3. (Note: PAE was added first followed by CMC.)

Table 1. The effect of carboxymethyl cellulose-polyamines on the strength of alpha cellulose handsheets.

Set No.	Additive, % based on fiber	CMC/PAE Ratio	Basis Wt., g/m^2	Thickness, μm	Apparent Density, g/cc	Dry Breaking Length, km	Moist Breaking Length, km	Moist Tensile Factor[c]	Wet Breaking Length, km (after 24 h soak)	Wet Tensile Factor[d]	Fluorescence Size, s
1	Blank controls (100% alpha pulp)		63.8	168	0.380	1.20	0.717	1.00	0.058	1.00	Instantaneous
2	PAE[a], 1.0; CMC[b], 0.4	0.4	63.0	161	0.392	2.18	1.420	1.98	0.602	10.38	Instantaneous
3	PAE, 1.0; CMC, 1.0	1.0	62.6	164	0.380	1.42	0.881	1.23	0.267	4.60	Instantaneous
4	PAE, 1.0; CMC, 2.0	2.0	62.8	168	0.375	1.44	0.872	1.22	0.555	9.57	Instantaneous
5	PAE, 2.5; CMC, 0.4	0.16	63.7	166	0.383	1.45	0.874	1.22	0.598	6.31	Instantaneous
6	PAE, 2.5; CMC, 1.0	0.4	62.3	155	0.402	2.62	1.730	2.41	0.901	15.53	Instantaneous
7	PAE, 2.5; CMC, 2.0	0.8	62.4	159	0.391	2.11	1.400	1.95	0.641	18.05	Instantaneous
8	PAE, 5.0; CMC, 0.4	0.08	63.0	166	0.379	1.39	0.871	1.21	0.294	5.06	Instantaneous
9	PAE, 5.0; CMC, 1.0	0.20	62.4	162	0.386	1.71	1.090	1.52	0.467	8.05	Instantaneous
10	PAE, 5.0; CMC, 2.0	0.40	62.4	154	0.404	2.81	1.910	2.66	1.020	17.58	Instantaneous
11	Control, CMC, 2.0	--	63.5	168	0.378	1.17	0.677	2.94	0.064	1.10	Instantaneous
12	Control, PAE, 2.5	--	61.9	166	0.372	1.25	0.731	1.02	0.142	2.45	Instantaneous
13	Control, PAE, 5.0	--	63.3	168	0.377	1.20	0.765	1.07	0.715	3.10	Instantaneous

[a]Polyamide polyamine epichlorohydrin.
[b]Carboxymethyl cellulose, low viscosity, D.S. = 0.7.
[c]Moist tensile of treated paper/moist tensile of untreated controls.
[d]Wet tensile of treated paper/wet tensile of untreated controls.

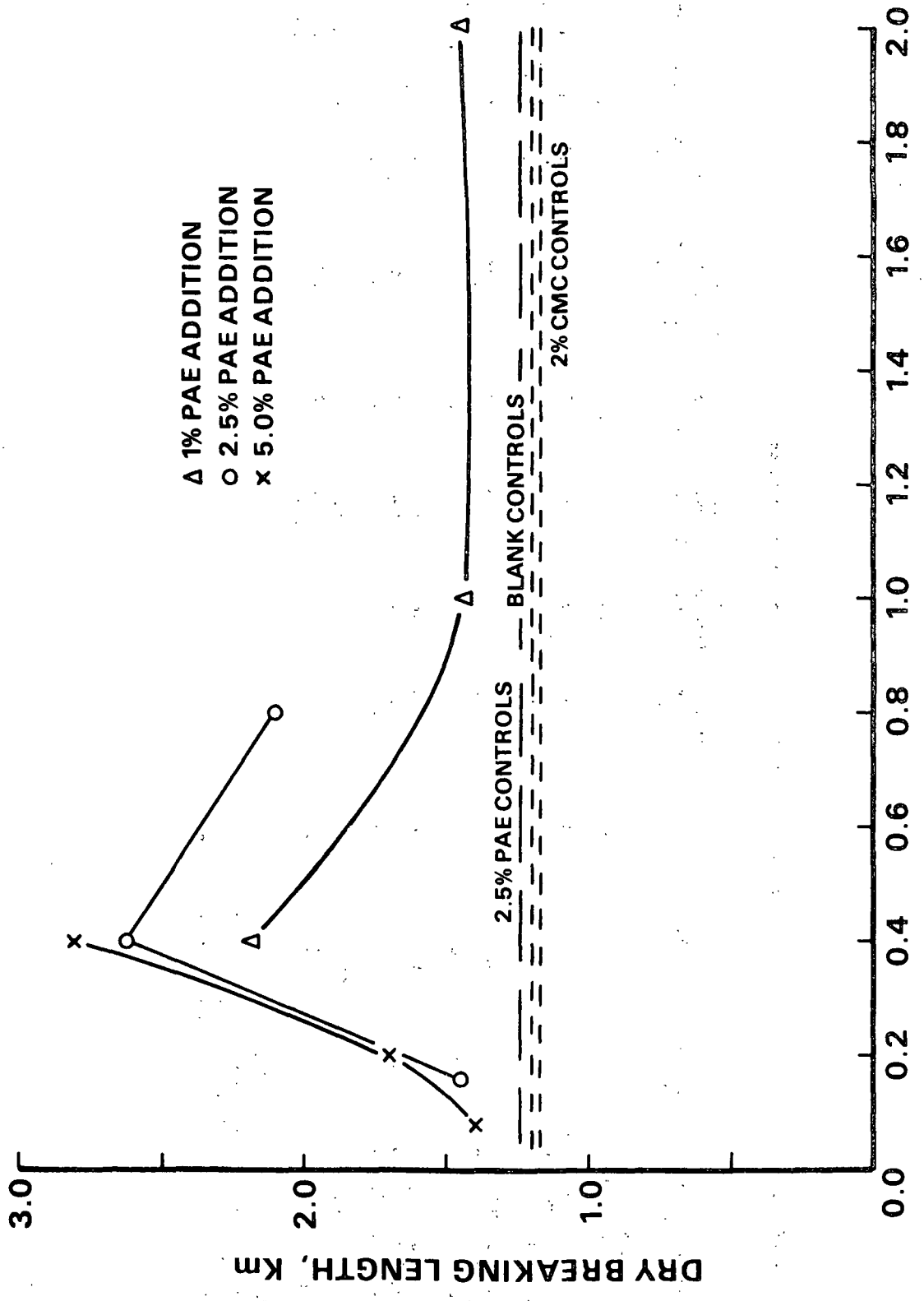


Figure 1. The effect of CMC/PAE ratio on dry breaking length (alpha pulp).

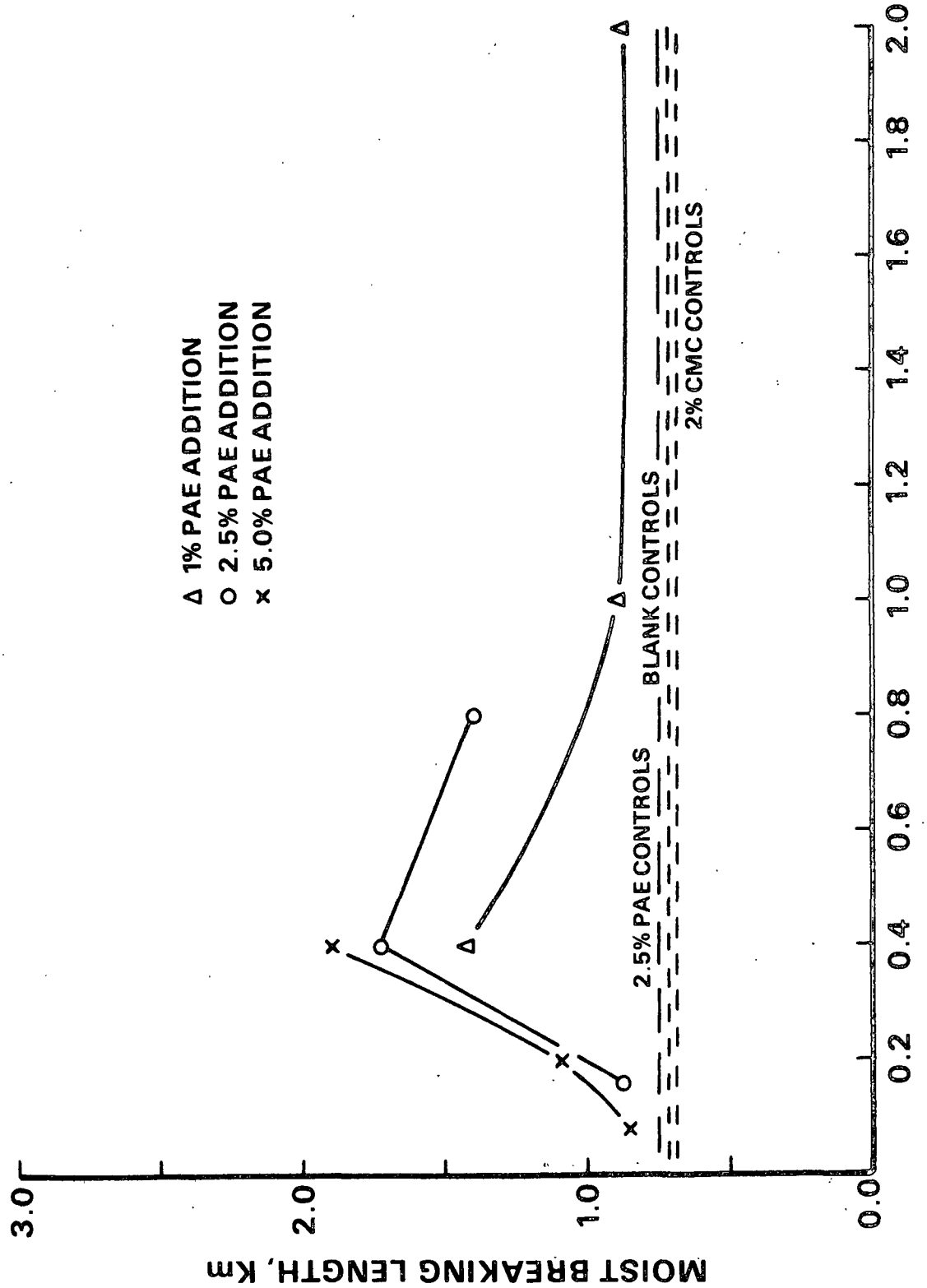


Figure 2. The effect of CMC/PAE ratio on moist breaking length (alpha pulp).

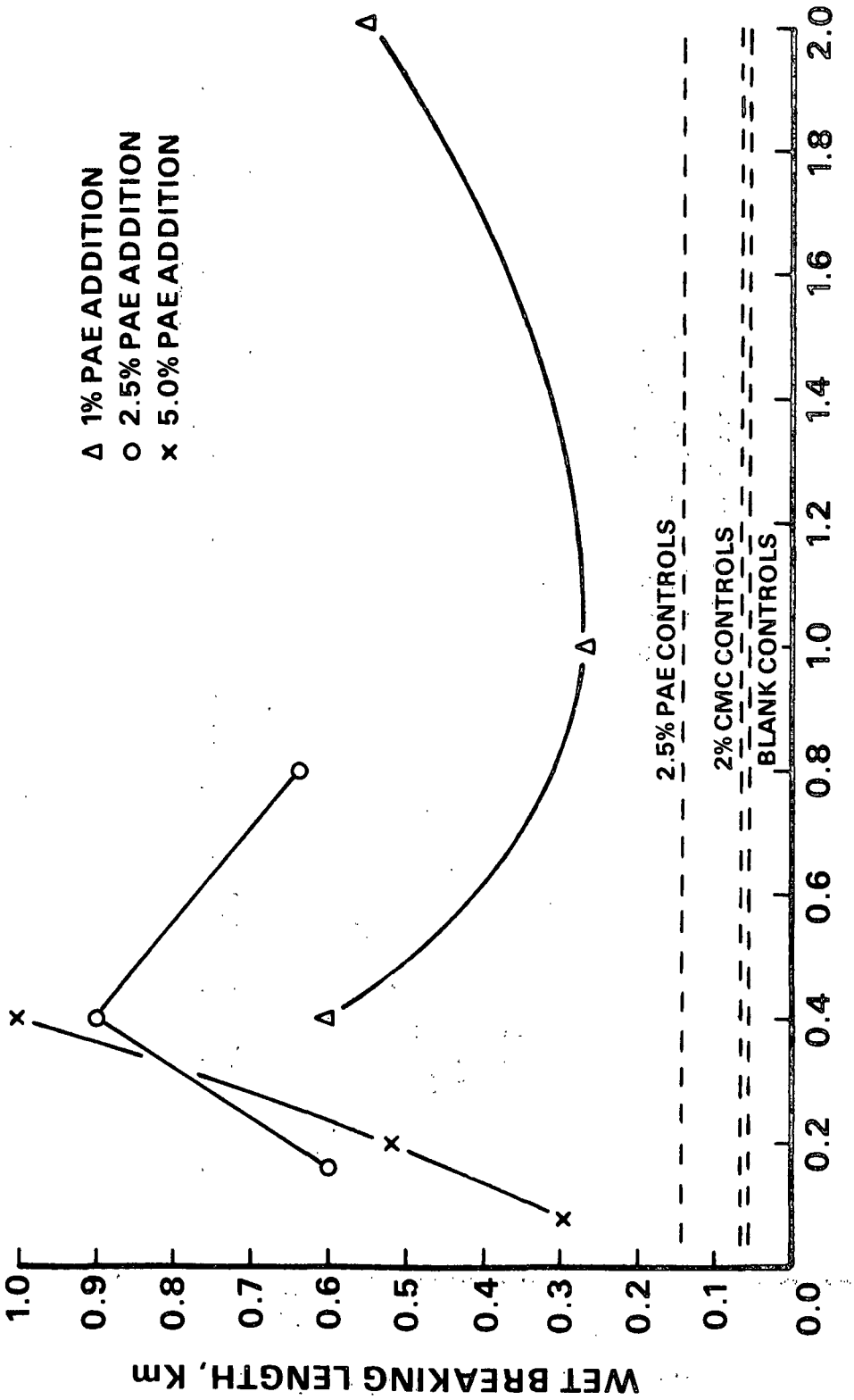


Figure 3. The effect of CMC/PAE ratio on wet breaking length (alpha pulp).

HANDSHEET STUDIES - SOFTWOOD UNBLEACHED KRAFT PULPS

Several series of experiments were undertaken employing southern pine unbleached kraft pulps of conventional yield. The pulps were prepared at the Institute from the same chip supply, and pertinent information covering these pulps is presented in Table 2. The pulps were beaten in tap water to 370 mL CSF and then classified to provide a final freeness of 735-760 mL CSF. The fines content (before classifying) was approximately 11%. The pulps were classified in order to avoid possible variations in fines retention due to the effects of the additive.

Table 2. Unbleached kraft pulps from southern pine (pulps prepared at the Institute).

Pulping Conditions and Pulp Properties	Cook No. 1	Cook No. 2
Charge, g, o.d.	6,000	8,000
Charge, g, a.d.	6,897	8,779
Water/wood ratio	4/1	4/1
Maximum temp., °C	173	173
Sulfidity, %	25.0	25.0
Effective alkali, %	16.0	16.0
Active alkali, %	18.3	18.3
Time to temperature, min	90	90
Time at temperature, min	To 1800 H Factor	To 1800 H Factor
Yield, %	48.8	47.2
Kappa No.	33.7	34.3
Fiber length		
Arithmetic av.	1.7 mm	1.8 mm
Weighted av.	2.2 mm	2.4 mm

Note: Chips from the above cooks were passed through a 12-inch Sprout-Waldron disk refiner at 0.009-inch clearance.

On the basis of information given in the literature (22, 23) and the results obtained with the alpha pulp, handsheets were prepared from the kraft pulp (cook No. 1) incorporating CMC/PAE, PVA/TMM, and PVA/PAE combinations. The PVA/TMM and PVA/PAE combinations were utilized without and with 1% of polyacrylic acid (mol. wt. 104,000) based on fiber weight. Addition levels of CMC/PAE were reduced from those employed in the high alpha pulp. For example, CMC/PAE combinations were used in this series at a maximum total addition of 2.1% based on fiber weight. As before, PAE and CMC were added separately, i.e., PAE followed by CMC. Results of an expanded testing program are recorded in Table 3. (Note: one handsheet equivalent to 630 g/m^2 was included in each set of this series for modulus measurements). Physical test properties as a function of total addition level are presented in Fig. 4-9.

Since sheet density can affect strength properties at equal basis weight, the decision was made to correct tensile properties to the density of the blank controls. The results are presented in Table 4, and the moist and wet tensile factors are presented in Fig. 10 and 11, respectively. The effect of relative humidity on sheet moisture content for the CMC/PAE series is shown in Fig. 12. A subsequent series examined the effects of CMC/PAE ratio at a constant addition level of 1%. Results are recorded in Table 5 and in Fig. 13-18. (Note: Since these series were not made in sequence, i.e., several months' time elapsed between tests and the supply of pulp from cook No. 1 was exhausted, it was necessary to use pulp from cook No. 2 in the last series). It should also be noted that pulp No. 2 was somewhat weaker than pulp No. 1 in spite of the fact that the yields, kappa numbers, and fiber lengths were quite similar. Additional work with CMC/PAE combinations was limited to a CMC/PAE ratio of 0.4. The first set of tests examined the effect of sizing agents on the efficiency of the CMC/PAE system, in which case the pH varied from 5 to 8-9.

Table 3. CMC-PAE combinations in classified softwood unbleached kraft pulp (pulp - cook No. 1, 48.8% yield; kappa No. 33.7).

Set No.	Additive, % based on fiber	CMC/PAE Ratio	Basis Wt., g/m^2	Thickness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	SD	TEA $kg\ m/m^2$	SD	Et kg/cm	SD	Stretch %	SD
14	Blank controls	--	63.1	161	0.390	3.22	0.145	2.56	0.382	261	11.3	1.84	0.177
15	Control, PAE, 0.5	--	63.5	164	0.387	4.01	0.645	--	--	287	25.2	--	--
16	Control, PAE, 1.5	--	64.8	162	0.400	5.08	0.174	5.98	0.521	313	4.8	2.78	0.157
17	Control, CMC, 0.4	--	61.7	156	0.396	3.31	0.216	2.58	0.572	289	12.9	1.79	0.264
18	PAE, 1.0; CMC, 0.4	0.4	62.9	149	0.423	7.18	0.635	9.52	1.541	394	28.8	3.29	0.269
19	PAE, 1.5; CMC, 0.6	0.4	63.0	147	0.429	7.43	0.300	9.32	0.422	371	6.2	3.54	0.170
20	PAE, 0.5; CMC, 0.2	0.4	64.0	153	0.418	6.33	0.358	4.04	0.436	356	13.7	3.17	0.333
21	PAE, 1.0; CMC, 0.25	0.25	63.2	152	0.416	6.37	0.220	4.23	0.295	353	28.2	3.22	0.186

Set No.	Additive, % based on fiber	Moist Strength Properties: Breaking Length km	SD	TEA $kg\ m/m^2$	SD	Et kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Wet Breaking Length km	SD	Wet Tensile Factor	In-Plane Moduli E_{Youngs}	E_{Shear}	Fluorescence Size, s
14	Blank controls	1.89	0.740	2.24	0.211	157	14.3	2.77	0.200	1.00	0.108	0.004	1.00	4.442	1.747	Instantaneous
15	Control, PAE, 0.5	2.37	0.161	--	--	102	16.2	--	--	1.25	0.900	0.078	8.33	--	--	Instantaneous
16	Control, PAE, 1.5	3.46	0.159	5.16	0.491	179	11.9	3.86	0.209	1.83	1.380	0.036	12.77	5.381	2.121	Instantaneous
17	Control, CMC, 0.4	1.79	0.264	2.28	0.135	154	9.1	2.80	0.146	0.98	0.099	0.010	0.92	4.778	1.974	Instantaneous
18	PAE, 1.0; CMC, 0.4	4.98	0.066	7.82	0.351	207	28.4	4.44	0.115	2.63	1.840	0.097	17.04	6.426	2.448	Instantaneous
19	PAE, 1.5; CMC, 0.6	5.07	0.285	7.94	0.811	180	14.7	4.67	0.190	2.68	2.120	0.110	19.63	6.756	2.501	Instantaneous
20	PAE, 0.5; CMC, 0.2	3.98	0.242	5.85	0.292	176	12.4	4.02	0.073	2.10	1.360	0.095	12.60	5.696	2.210	Instantaneous
21	PAE, 1.0; CMC, 0.25	4.52	0.139	6.94	0.631	168	18.0	4.43	0.259	2.39	1.740	0.049	16.11	6.057	2.278	Instantaneous

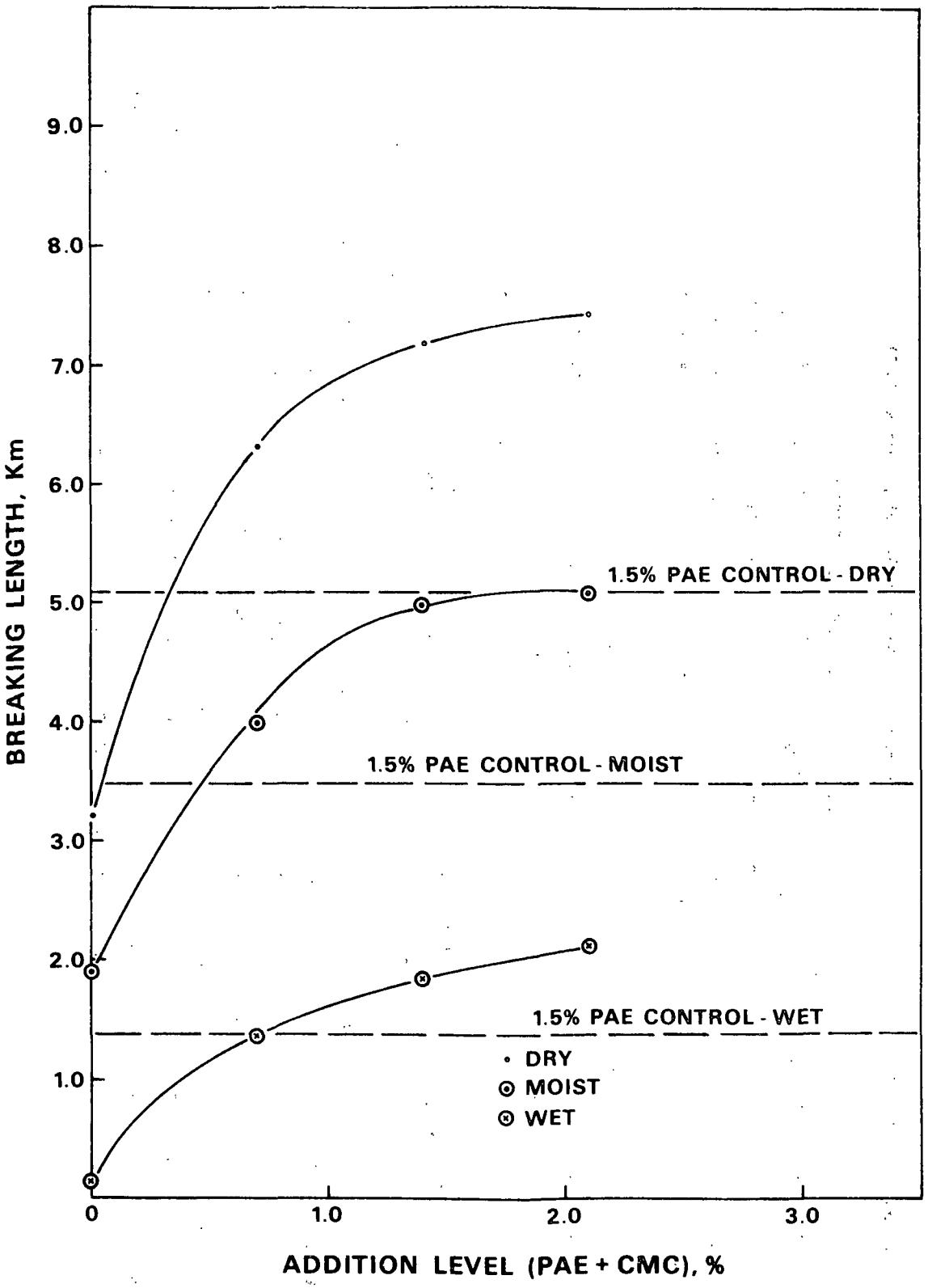


Figure 4. The effect of CMC/PAE addition level on breaking length at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield, kappa No. 33.7).

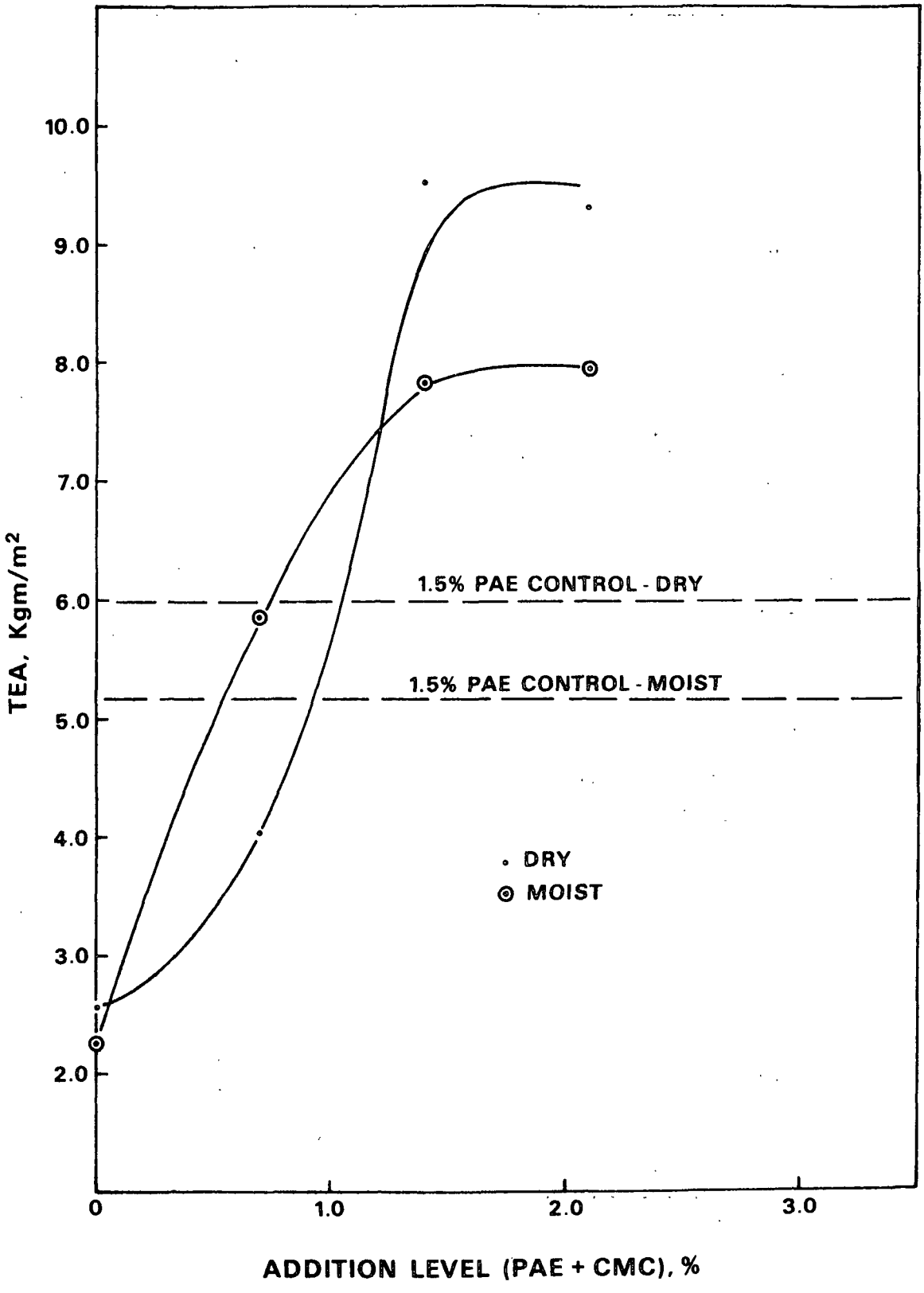


Figure 5. The effect of CMC/PAE addition level on TEA at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

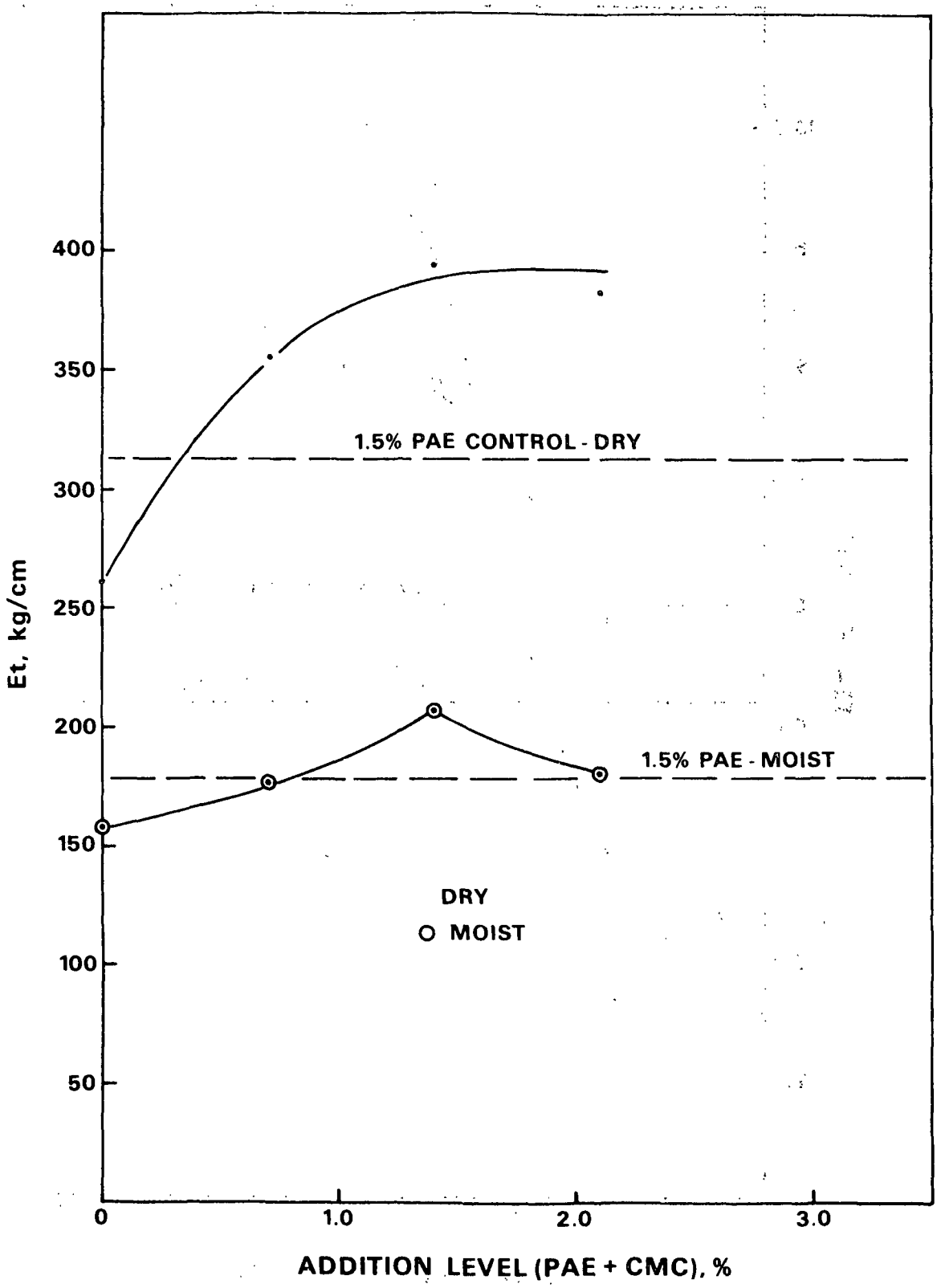


Figure 6. The effect of CMC/PAE addition level on extensional stiffness at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

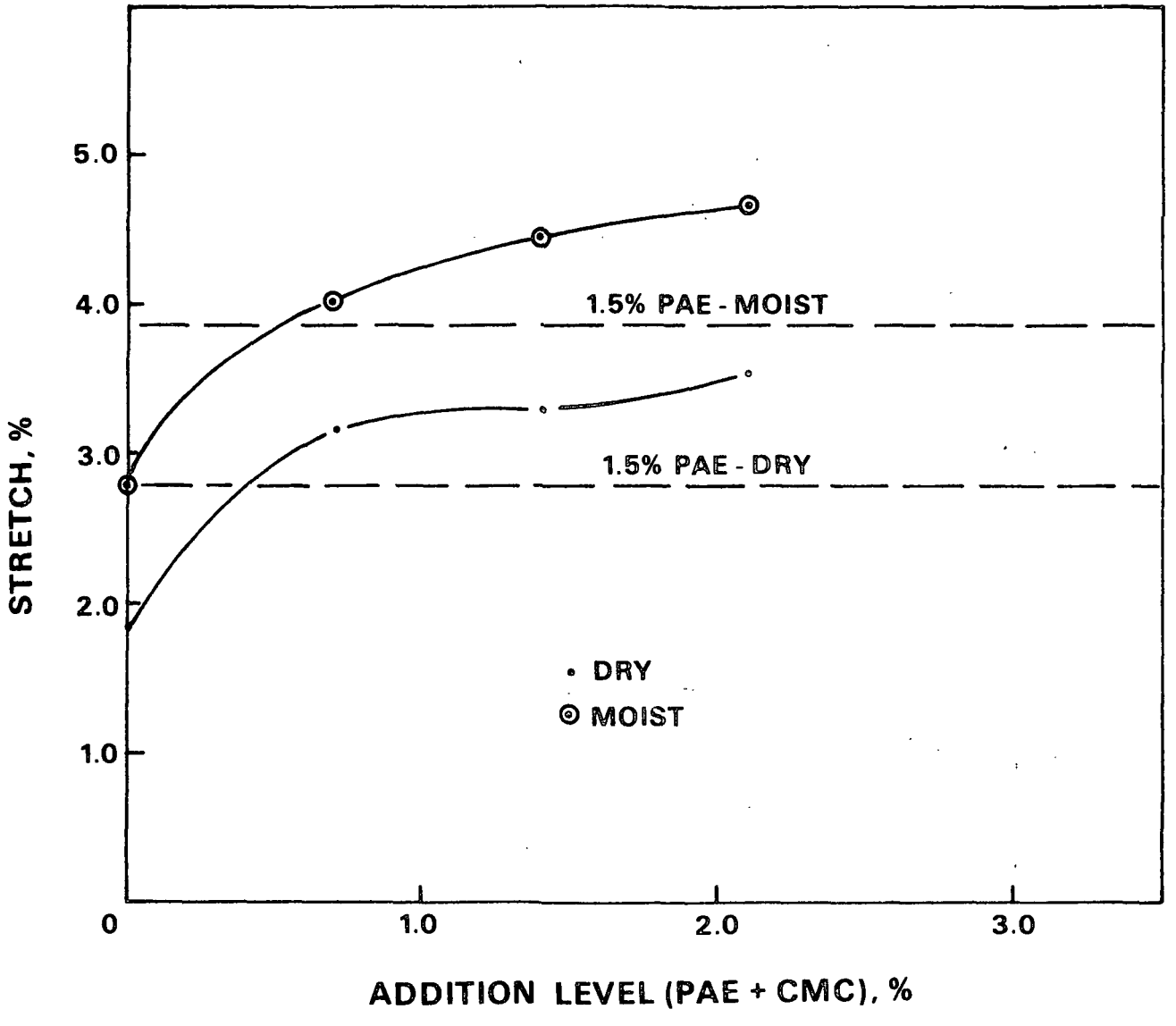


Figure 7. The effect of CMC/PAE addition level on stretch at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

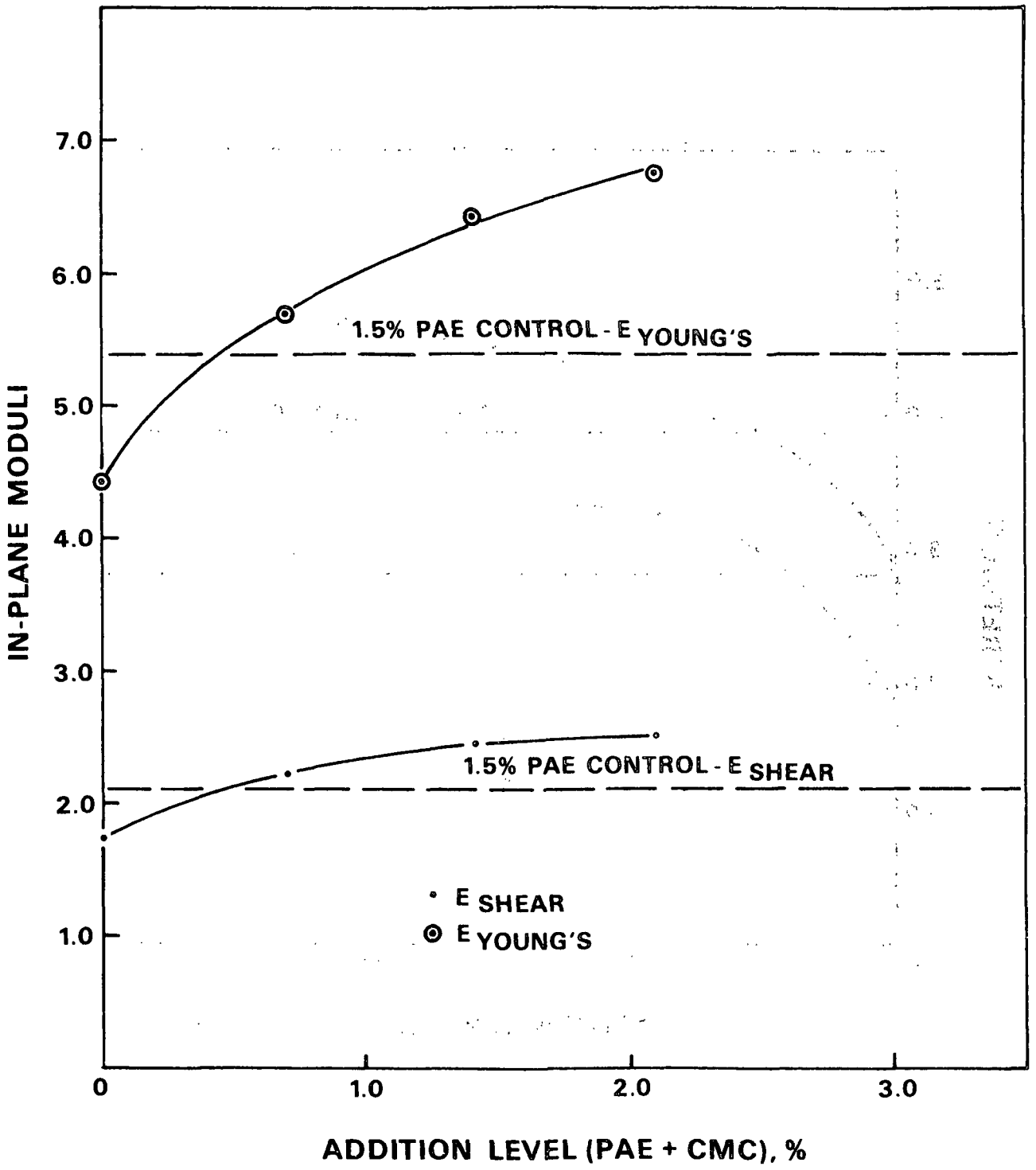


Figure 8. The effect of CMC/PAE addition level on in-plane moduli at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

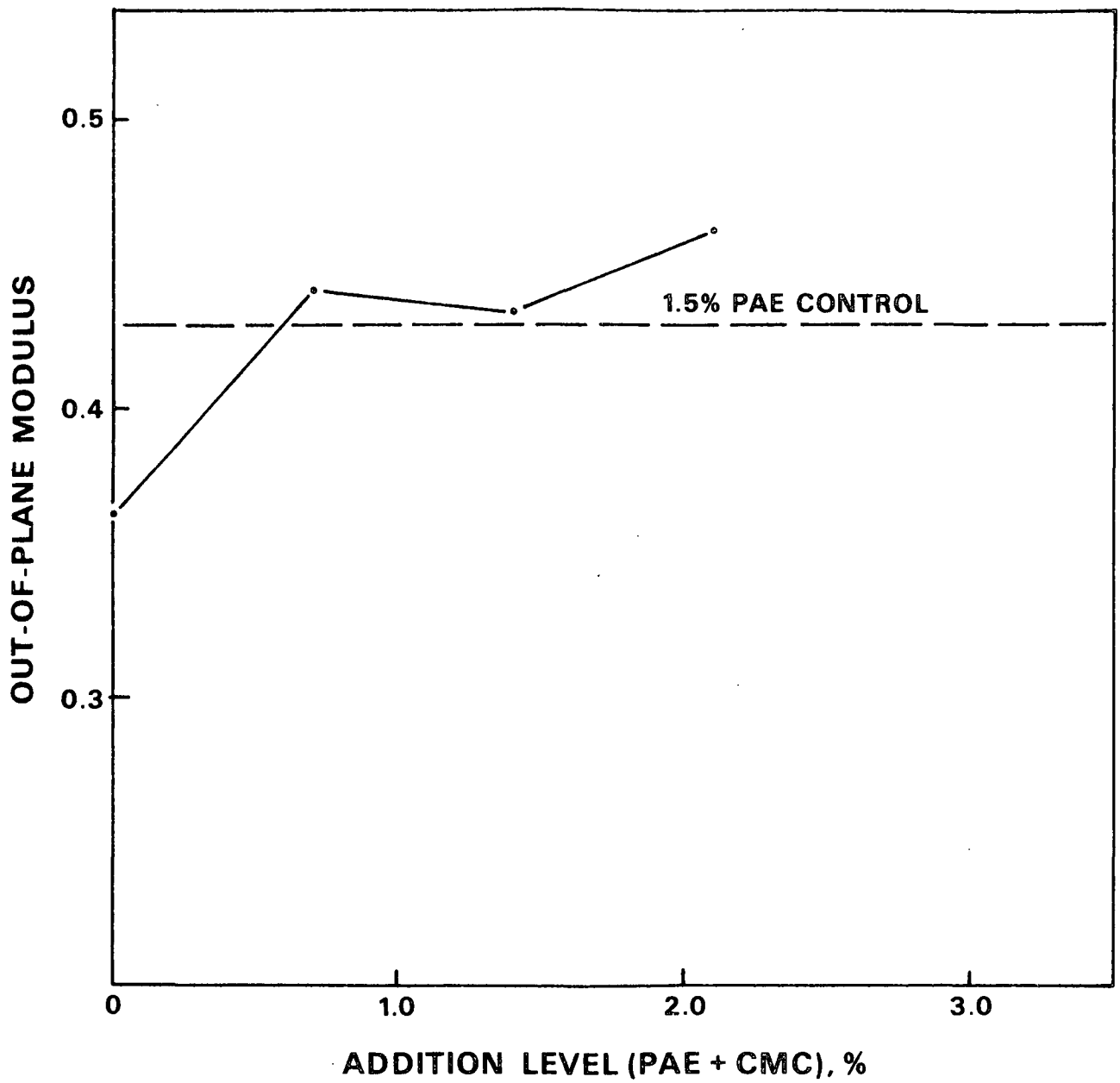


Figure 9. The effect of CMC/PAE addition level on out-of-plane modulus at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

Table 4. Tensile properties corrected for differences in sheet density. (Classified unbleached kraft pulp - cook No. 1, 48.8% yield; kappa No. 33.7).

Set No.	Additives, % based on fiber	CMC/PAE Ratio	Basis Weight, g/m^2	Apparent Density, g/cc	Dry Breaking Length, km		Moist Breaking Length, km		Moist Tensile Factor		Wet Breaking Length, km		Wet Tensile Factor	
					Uncor	Cor[a]	Uncor	Cor[a]	Uncor	Cor[a]	Uncor	Cor[a]	Uncor	Cor[a]
14	Blank control	--	63.1	0.390	3.22	3.22	1.89	1.89	1.0	1.0	0.108	0.108	1.0	1.0
16	Control, PAE, 1.5	--	64.8	0.400	5.08	4.95	3.46	3.37	1.83	1.78	1.38	1.38	12.77	12.12
17	Control, CMC, 0.4	--	61.7	0.396	3.31	3.26	1.86	1.83	0.98	0.97	0.099	0.097	0.92	0.90
18	PAE,1.0; CMC, 0.4	0.4	62.9	0.423	7.18	6.60	4.98	4.58	2.63	2.42	1.84	1.69	17.04	15.65
19	PAE,1.5; CMC, 0.6	0.4	63.0	0.429	7.43	6.76	5.07	4.61	2.68	2.44	2.12	1.93	19.63	17.87
20	PAE,0.5; CMC, 0.2	0.4	64.0	0.418	6.33	5.90	3.98	3.71	2.10	1.96	1.36	1.27	12.60	11.76
21	PAE,1.0; CMC, 0.25	0.25	63.2	0.416	6.37	5.98	4.52	4.24	2.39	2.24	1.74	1.63	16.11	15.09

[a]Corrected to the density of the blank control.

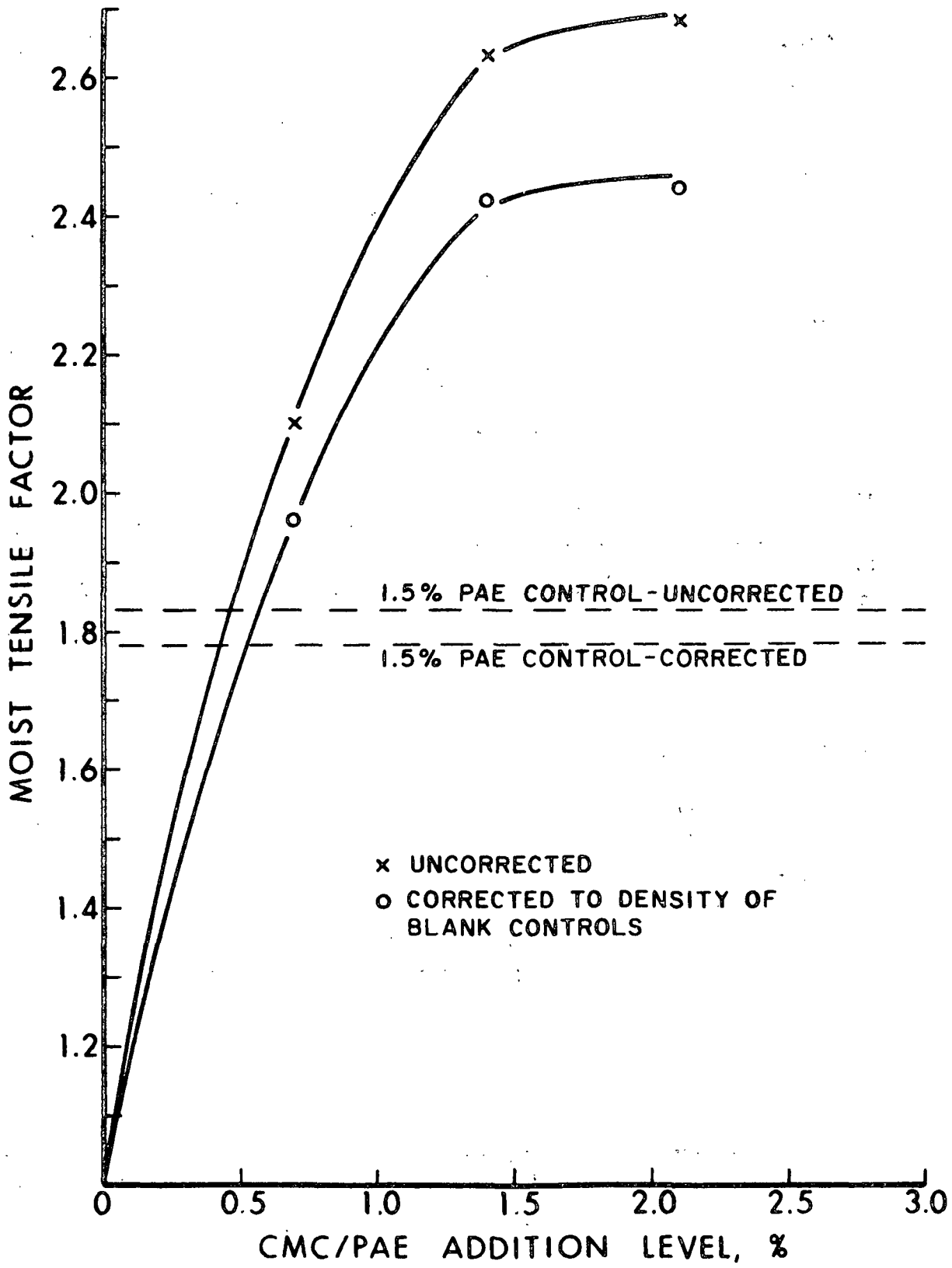


Figure 10. The effect of CMC/PAE addition level on moist tensile factor at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

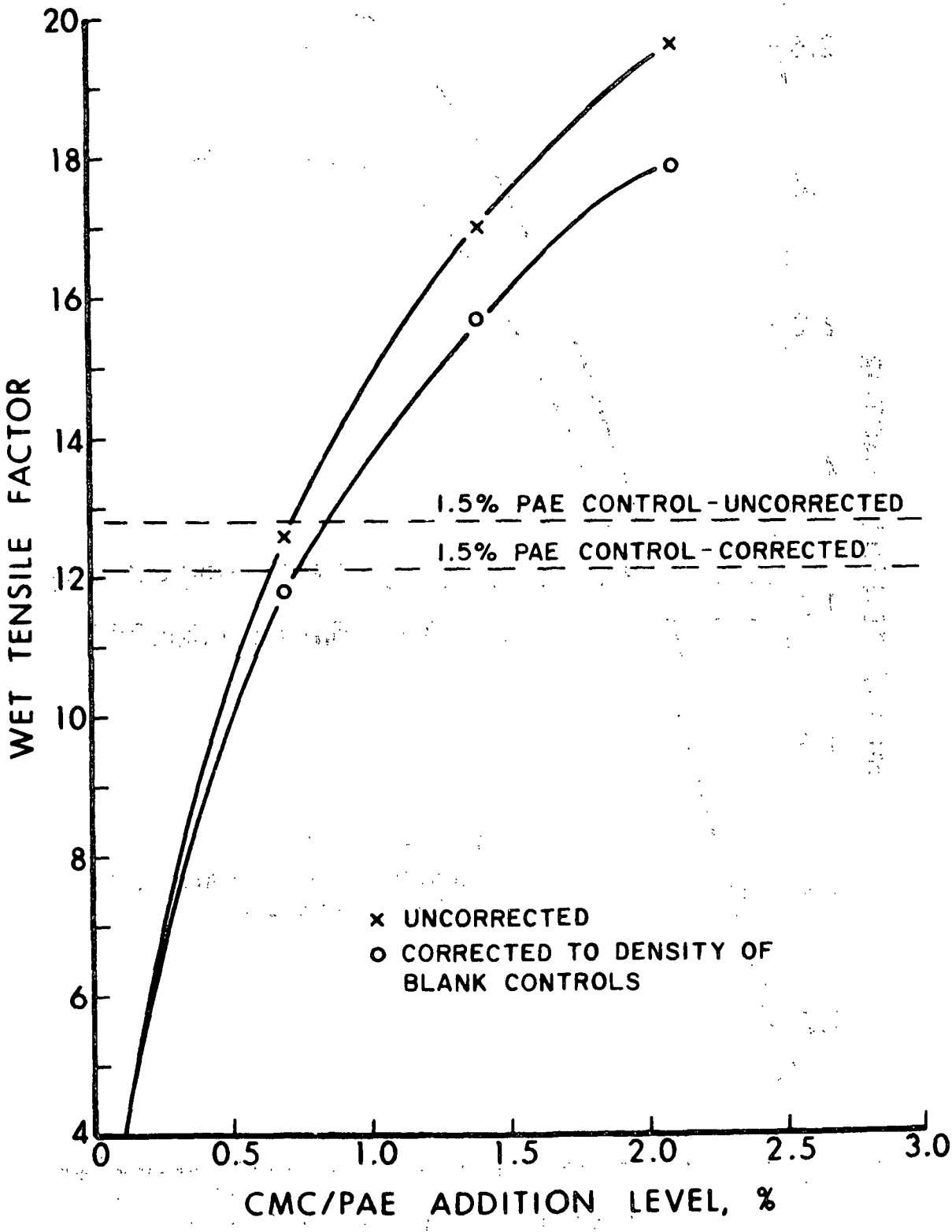


Figure 11. The effect of CMC/PAE addition level on wet tensile factor at a CMC/PAE ratio of 0.4 (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

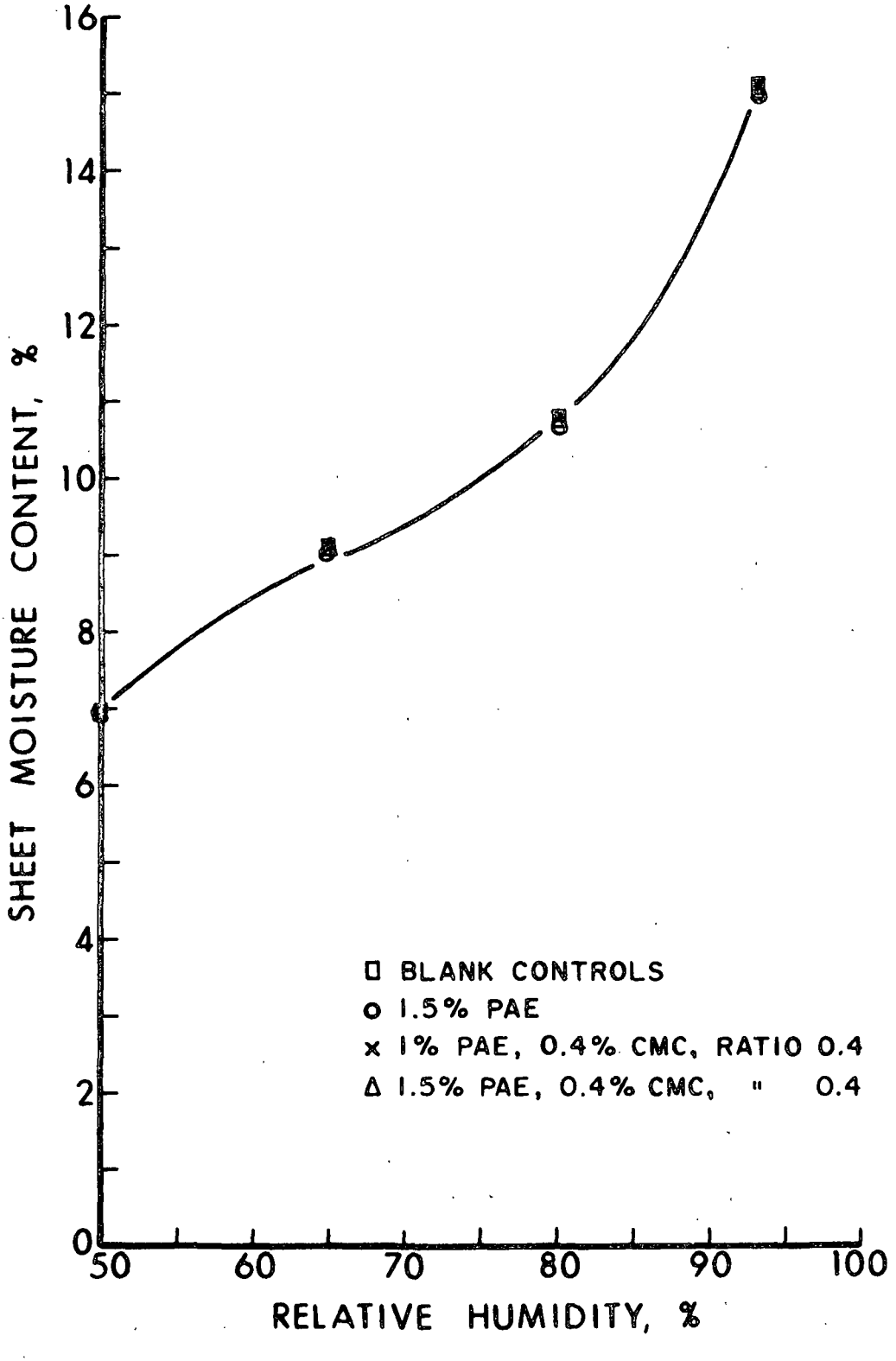


Figure 12. The effect of relative humidity on sheet moisture content (classified unbleached kraft - 48.8% yield; kappa No. 33.7; CMC/PAE combinations).

Table 5. The effect of CMC/PAE ratio on strength properties (classified unbleached kraft - cook No. 2, 47.2% yield; kappa No. 34.3).

Set No.	Additives, % based on fiber	CMC/PAE Ratio	Basis Wt., g/m²	Thickness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et[a] kg/cm	SD	Stretch %	SD
22	Blank controls	--	60.9	158	0.386	2.90	0.165	2.20	0.286	209	17.4	1.87	0.153
23	Controls, PAE, 1.0	--	63.2	163	0.388	4.47	0.358	4.99	0.653	273	12.3	2.69	0.151
24	PAE, 0.8; CMC, 0.2	0.25	68.4	169	0.406	6.08	0.313	8.30	0.815	368	8.6	3.12	0.105
25	PAE, 0.71; CMC, 0.29	0.40	62.2	155	0.401	5.66	0.660	6.68	1.365	333	30.7	2.96	0.296
26	PAE, 0.59; CMC, 0.41	0.70	59.5	148	0.402	5.68	0.397	6.93	0.986	306	7.8	3.18	0.263
27	PAE, 0.5; CMC, 0.50	1.00	65.9	161	0.410	5.51	0.584	7.32	0.727	349	49.0	3.08	0.149

Set No.	Additive, % based on fiber	Moist Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et[a] kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Wet Breaking Length km	SD	Wet Tensile Factor
22	Blank controls	1.34	0.100	1.45	0.152	96.5	11.0	2.71	0.178	1.00	0.06	0.006	1.00
23	Controls, PAE, 1.0	1.76	0.189	3.58	0.627	114	13.9	3.80	0.368	1.31	0.75	0.034	12.5
24	PAE, 0.8; CMC, 0.2	1.94	9.066	4.39	0.398	109	3.20	4.03	0.321	1.45	1.34	0.075	22.3
25	PAE, 0.71; CMC, 0.29	1.86	0.086	4.55	0.367	95.5	5.75	4.46	0.210	1.39	1.50	0.108	25.0
26	PAE, 0.59; CMC, 0.41	1.71	0.107	3.98	0.477	93.4	3.45	4.23	0.214	1.28	1.40	0.066	23.3
27	PAE, 0.5; CMC, 0.50	1.91	0.215	4.84	0.671	118	4.50	4.34	0.174	1.42	1.32	0.152	22.0

[a]Extensional stiffness.

NOTE: Sizing (water drop test) all instantaneous.

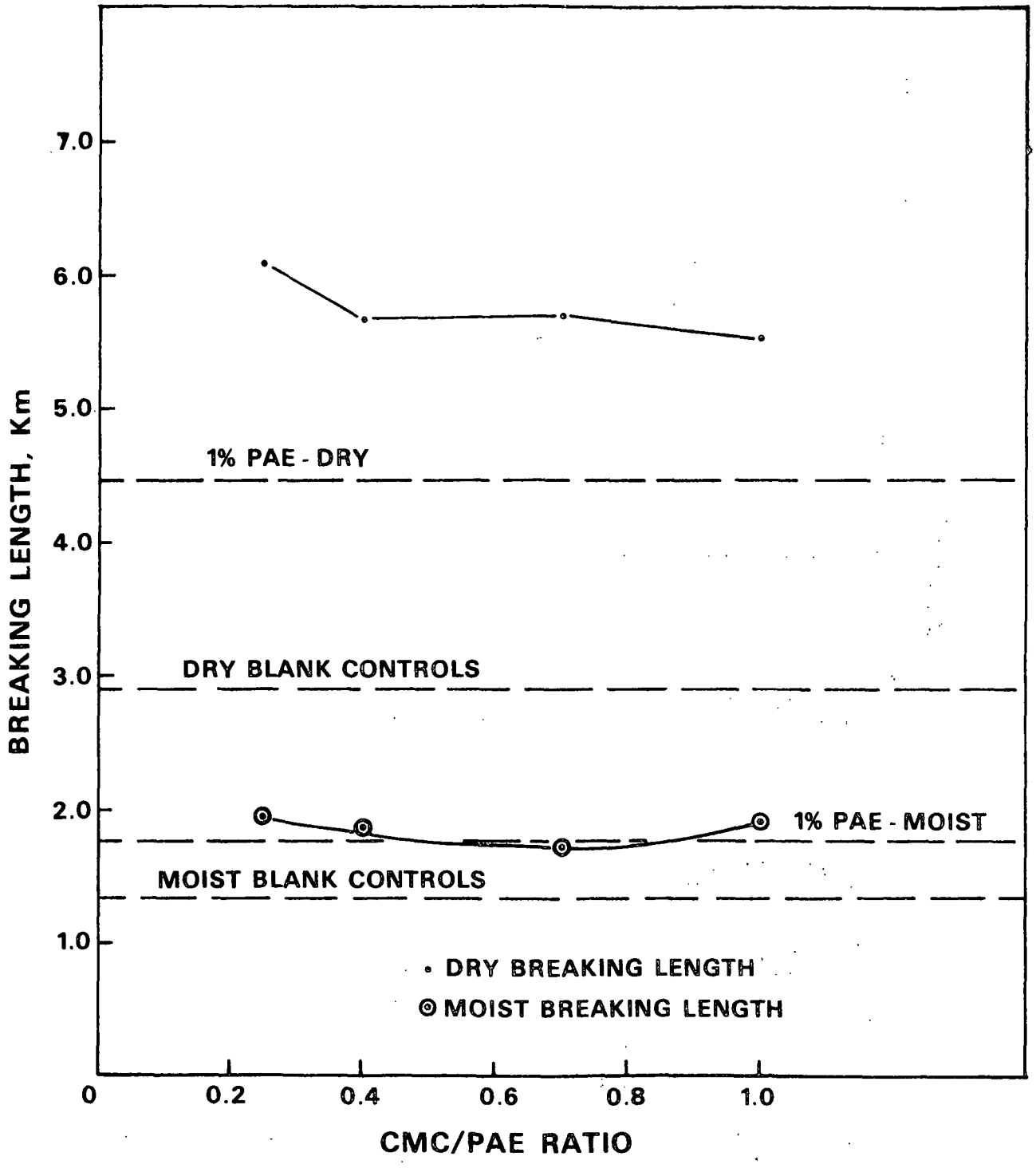


Figure 13. The effect of CMC/PAE ratio on breaking length at 1% addition level (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

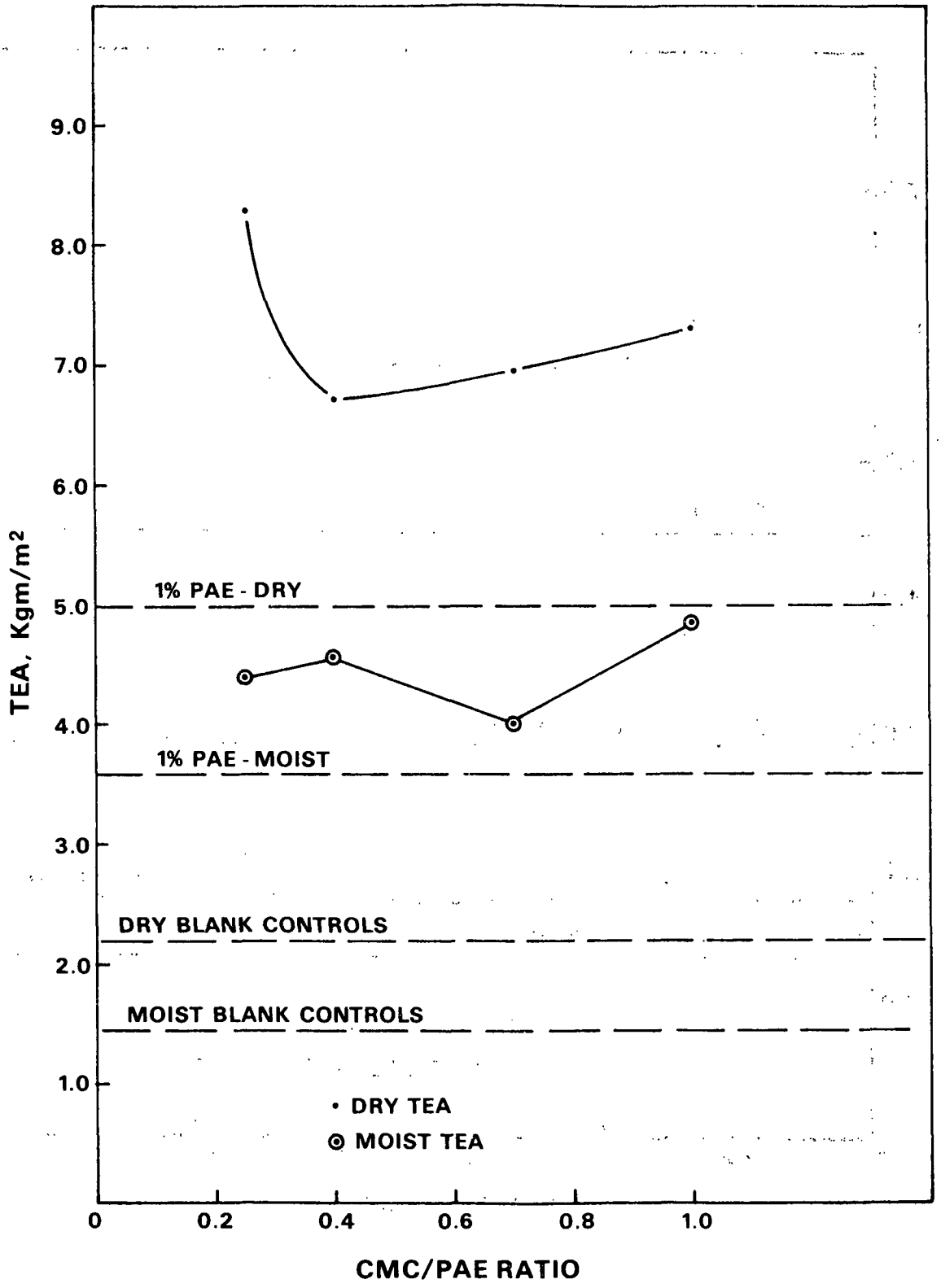


Figure 14. The effect of CMC/PAE ratio on tensile energy absorption at 1% addition level (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

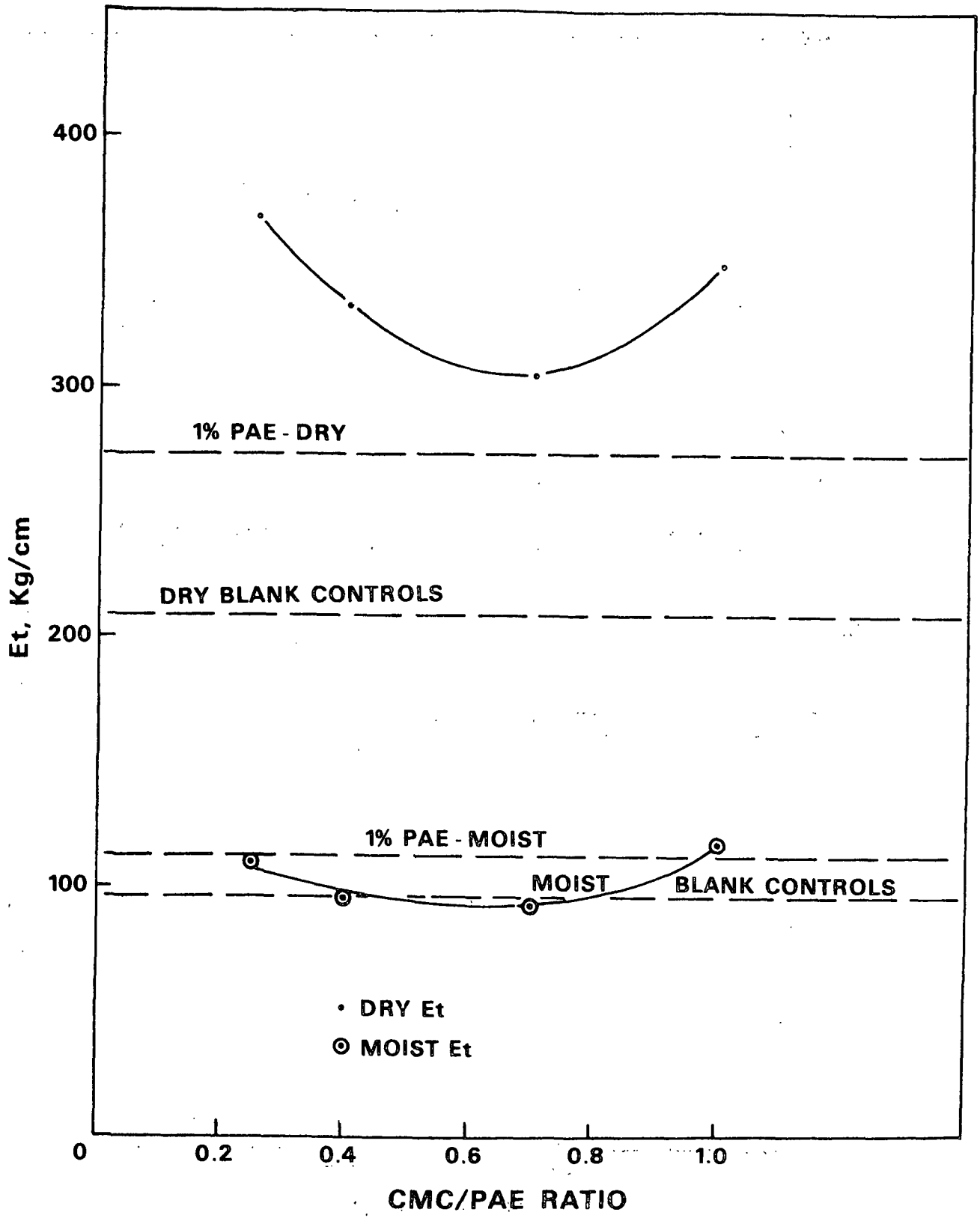


Figure 15. The effect of CMC/PAE ratio on extensional stiffness at 1% addition level (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

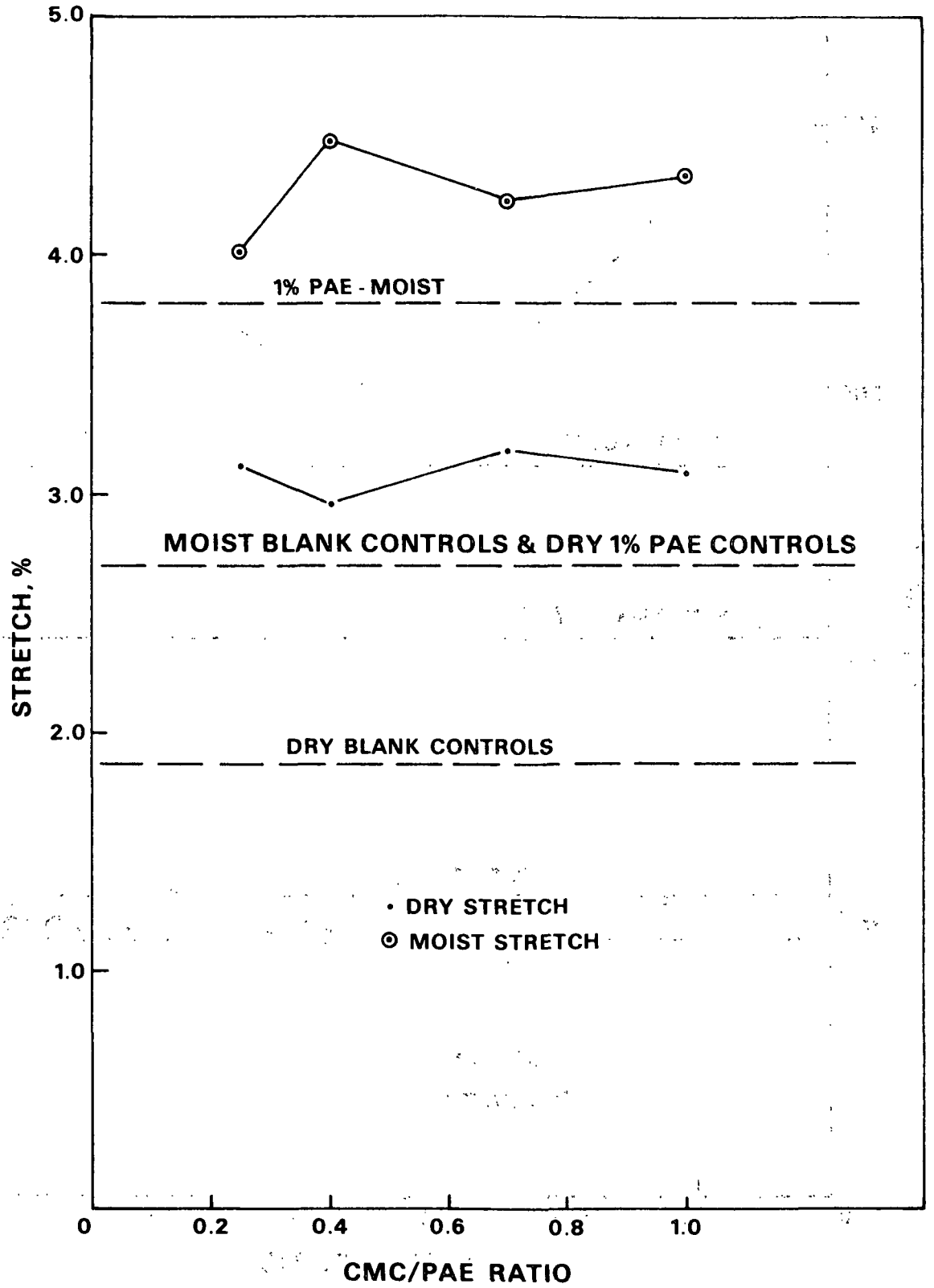


Figure 16. The effect of CMC/PAE ratio on stretch at 1% addition level (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

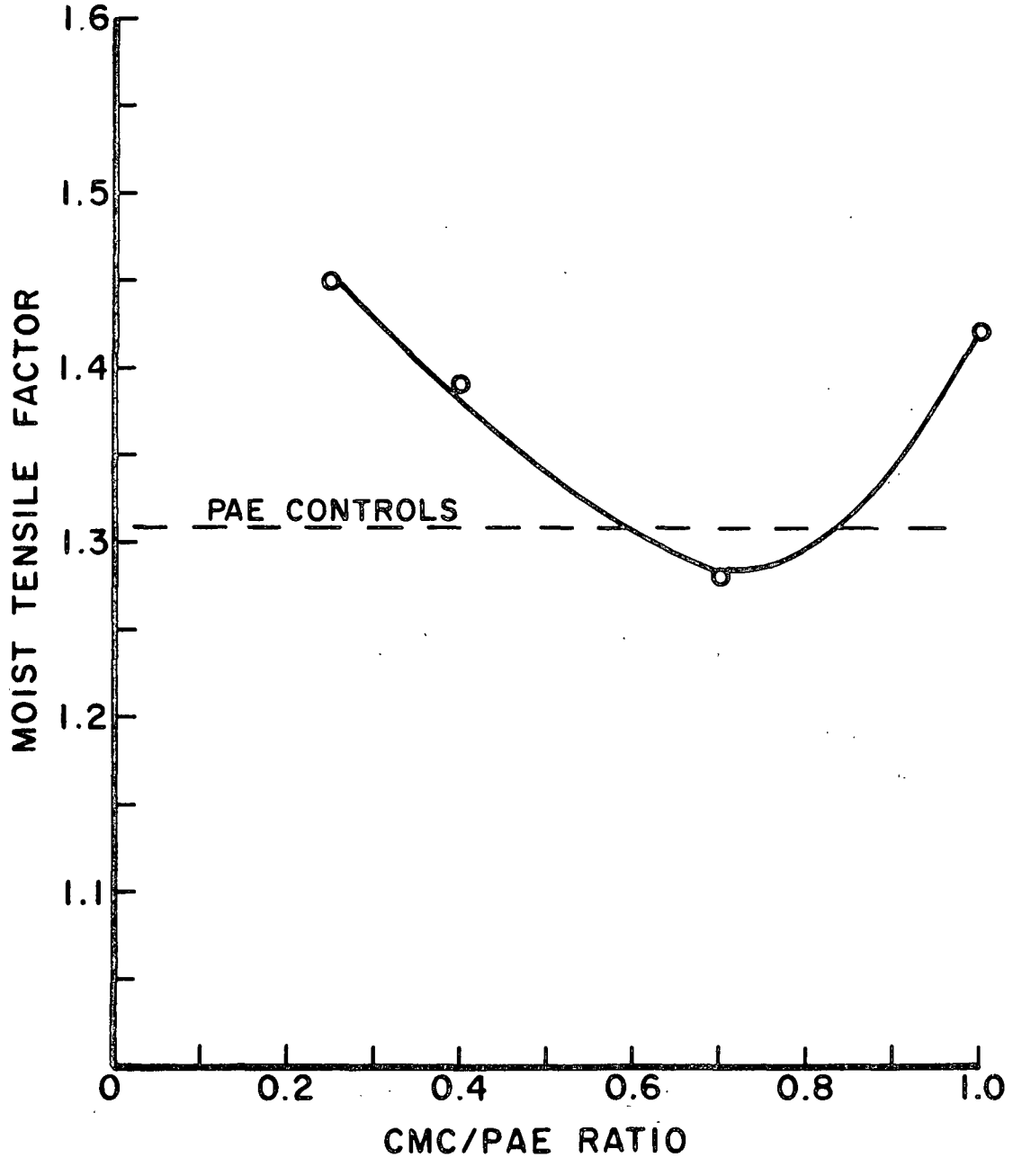


Figure 17. The effect of CMC/PAE ratio on moist tensile factor at 1% addition level (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

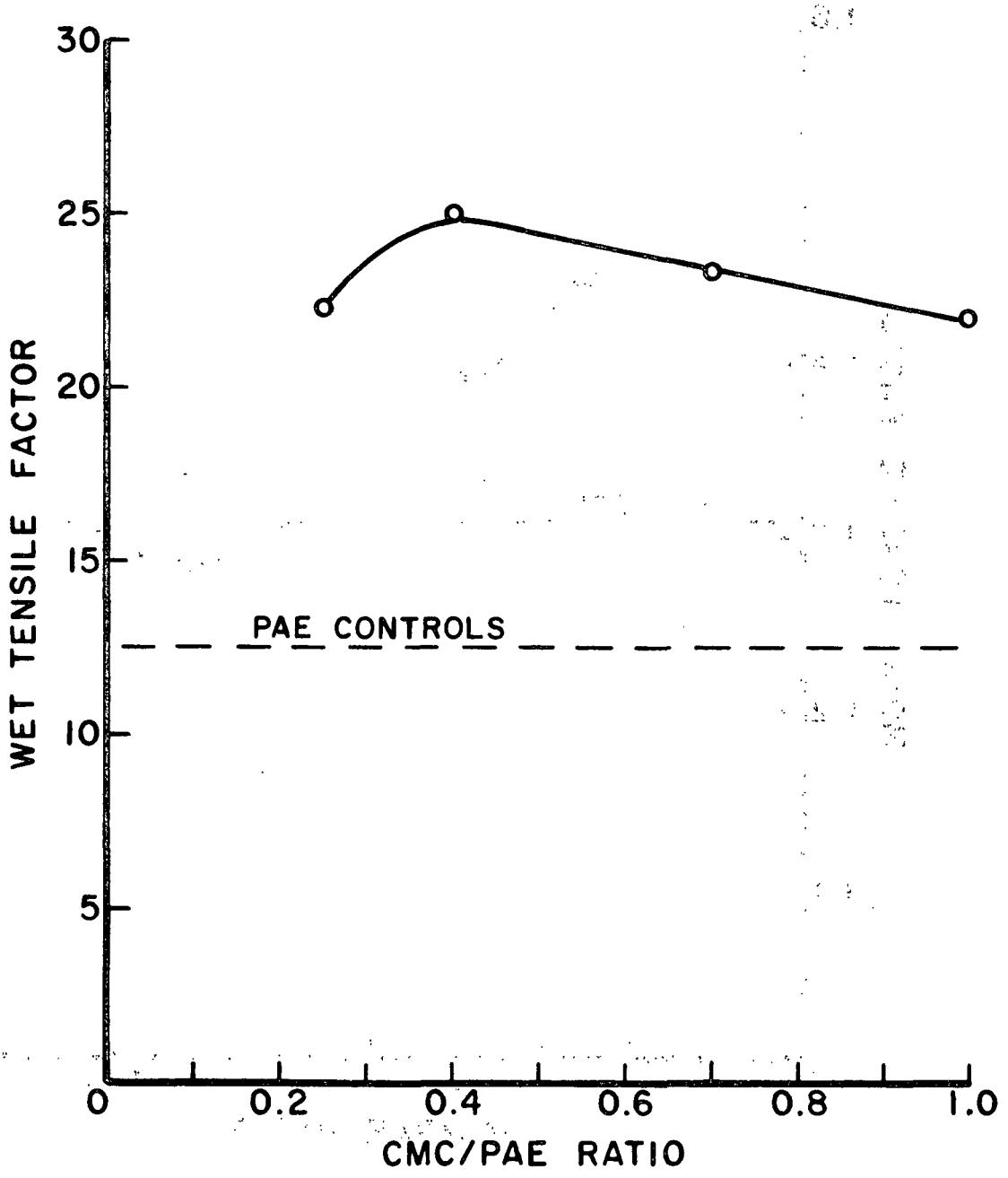


Figure 18. The effect of CMC/PAE ratio on wet tensile factor at 1% addition level (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

recorded in Table 6. The final set of experiments with CMC/PAE examined briefly the effect of fiber fines on polymer effectiveness, in which case the results are presented in Table 7.

In separate studies, 1:1 blends by weight of PVA:TMM and PVA:PAE were used at total additions of 0.3, 0.5, and 1.0% based on fiber weight. When used, a polyacrylic acid (mol. wt. 104,000) was used at an arbitrary addition level of 1% based on fiber. The polyacrylic acid was used in an effort to promote covalent bonding through ester formation by reaction with hydroxyl groups associated with TMM, PVA, PAE or possibly directly with cellulose itself. Results for the PVA-TMM series are presented in Table 8 and Fig. 19-31. Results for the PVA/PAE series are presented in Table 9 and Fig. 32-44. The effect of relative humidity on sheet moisture content for the PVA/TMM and PVA/PAE series are presented in Fig. 45 and 46.

Since, in general, the results obtained with PVA/PAE/PAA combinations showed greater potential than the PVA/TMM/PAA combinations, the decision was made to pursue combinations incorporating PAE and PAA with and without the third polymer. The decision was also made to reduce the amount of polyacrylic acid used in these mixtures by an order of magnitude, i.e., from 1.0 to 0.1% based on fiber. This change was made for several reasons. First of all, a control containing 0.5% of PAE and 1.0% of PAA without PVA (set 58) provided rather substantial improvements in tensile properties, but the improvements were not as great as those obtained when the polyvinyl alcohol was included in the blend. Hence, rather extensive studies were carried out with PVA:PAE blends with and without PAA. However, in subsequent work, there was some indication that less polyacrylic acid was needed, bearing in mind that the additive combinations do

Table 6. The effect of sizing agents on the efficiency of CMC/PAE combinations (classified unbleached kraft - cook No. 2, 47.2% yield; kappa No. 34.3).

Set No.	Additives, % based on fiber	Basis Wt., g/m^2	Thickness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	Dry SD	Dry Et[c] kg/cm	Dry Et SD	Moist Strength Properties: Breaking Length km	Moist SD	Moist Et[c] kg/cm	Moist Et SD	Moist Tensile Factor	Wet Breaking Length km	Wet SD	Wet Tensile Factor	Sizing (Water Drop Test), s
22	Blank controls[a]	60.9	158	0.386	2.90	0.165	209	17.4	1.34	0.100	96.5	11.0	1.0	0.06	0.006	1.0	Instantaneous
23	Controls, PAE, 1.0[a]	63.2	163	0.388	4.47	0.358	273	12.3	1.76	0.189	114	13.9	1.31	0.75	0.034	12.5	Instantaneous
28	PAE,1.0; CMC, 0.4[a]	63.9	157	0.406	6.63	0.471	344	20.7	3.44	0.133	124	16.4	2.57	1.24	0.049	20.7	Instantaneous
29	PAE,1.0; CMC, 0.4; alum, 1.0; dispersed rosin size, 0.5[b]	65.7	162	0.407	5.29	0.430	345	17.1	3.15	0.310	143	16.5	2.35	1.22	0.118	20.3	1800+
30	PAE,1.0; CMC, 0.4; alkyl succinic anhydride, 0.25[a]	62.3	148	0.421	5.86	0.662	326	31.9	3.32	0.315	124	18.8	2.48	1.05	0.113	16.7	1800+

[a] pH 8-9.
[b] pH 5.0-5.2.
[c] Extensional stiffness.

Table 7. A comparison of whole and classified pulps with respect to additive effectiveness (softwood unbleached kraft - cook No. 2, 47.2% yield; kappa No. 34.3).

Set No.	Additives, % based on fiber	Basis Wt., g/m²	Thickness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD
					Unclassified Pulp							
31	Blank controls	63.2	148	0.426	4.30	0.219	3.59	0.366	326	11.7	2.40	0.114
32	Controls, PAE, 1.0	63.1	146	0.431	6.42	0.412	6.52	0.283	345	38.3	3.33	0.217
33	PAE, 1.0; CMC, 0.4	64.5	146	0.443	6.74	0.308	7.69	0.656	379	9.5	3.51	0.202
					Classified Pulp							
22	Blank controls	60.9	158	0.386	2.90	0.165	2.20	0.286	209	17.4	1.87	0.153
23	Controls, PAE, 1.0	63.2	163	0.388	4.47	0.358	4.99	0.653	273	12.3	2.69	0.151
28	PAE, 1.0; CMC, 0.4	63.9	157	0.406	6.63	0.471	8.72	0.810	344	20.7	3.39	0.160

Set No.	Additives, % based on fiber	Moist Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Wet Breaking Length km	SD	Wet Tensile Factor
						Unclassified Pulp							
31	Blank controls	2.30	0.118	3.52	0.304	148	8.0	3.78	0.156	1.00	0.115	0.005	1.0
32	Controls, PAE, 1.0	3.69	0.095	6.65	0.289	140	10.1	4.99	0.077	1.60	1.180	0.033	10.3
33	PAE, 1.0; CMC, 0.4	4.14	0.168	9.80	0.199	152	10.8	5.25	0.182	1.80	1.280	0.044	11.1
						Classified Pulp							
22	Blank controls	1.34	0.100	1.45	0.152	96.5	11.0	2.71	0.178	1.00	0.060	0.006	1.0
23	Controls, PAE, 1.0	1.76	0.187	3.58	0.627	114	13.9	3.80	0.368	1.31	0.150	0.034	12.5
28	PAE, 1.0; CMC, 0.4	3.44	0.133	7.52	0.452	124	16.4	4.76	0.093	2.57	1.240	0.049	20.7

NOTE: Sizing (water drop test) was instantaneous in all cases.

Table 8. PVA/TMM combinations in classified softwood unbleached kraft pulp with and without polyacrylic acid (pulp - cook No. 1 48.8% yield; kappa No. 33.7).

Set No.	Additives, % based on fiber	Oven Aging, hours at 105°C	Basis Wt., g/m²	Thickness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD
14	Blank controls	--	63.1	161	0.390	3.22	0.145	2.56	0.382	261	11.3	1.84	0.177
34	Blank controls	24	63.6	162	0.391	3.41	0.261	--	--	240	17.2	1.98	0.200
35	Controls:alum, 0.75	--	63.8	163	0.391	3.20	0.300	2.55	0.597	268	26.0	1.84	0.232
36	Controls:PVA[a], 1.0, alum, 0.75	--	61.7	160	0.386	2.88	0.200	1.90	0.306	246	20.9	1.67	0.146
37	Controls:TMM[b] 0.5, alum, 0.75	--	64.1	160	0.401	3.51	0.151	3.08	0.471	278	14.6	2.01	0.209
38	Controls:PAA[c],1.0	--	61.8	157	0.392	3.13	0.156	2.52	0.314	236	15.3	2.00	0.160
39	Controls:PAA,1.0	24	64.2	164	0.392	3.25	0.263	2.46	0.695	266	18.3	1.82	0.322
40	1:1 PVA:TMM, 0.3, alum, 0.75	--	63.0	161	0.392	3.55	0.176	3.06	0.566	280	10.6	2.06	0.278
41	1:1 PVA:TMM, 0.5, alum, 0.75	--	59.0	155	0.381	4.71	0.222	4.66	0.333	268	14.2	2.56	0.128
42	1:1 PVA:TMM, 1.0, alum, 0.75	--	65.1	164	0.396	4.99	0.456	6.05	1.16	333	23.4	2.84	0.317
43	1:1 PVA:TMM, 0.3, alum, 0.75, PAA, 1.0	--	64.4	164	0.393	3.18	0.095	3.93	0.341	264	11.5	2.32	0.194
44	1:1 PVA:TMM, 0.5, alum, 0.75, PAA, 1.0	--	65.2	163	0.400	4.21	0.238	4.38	0.702	287	15.8	2.39	0.249
45	1:1 PVA:TMM, 1.0, alum, 0.75, PAA, 1.0	--	62.5	157	0.397	4.96	0.404	5.46	0.894	292	17.6	2.66	0.244
46	1:1 PVA:TMM, 0.3, alum, 0.75, PAA, 1.0	24	63.4	160	0.395	4.36	0.334	4.39	0.814	279	15.1	2.38	0.254
47	1:1 PVA:TMM, 0.5, alum, 0.75, PAA, 1.0	24	64.1	160	0.402	4.67	0.214	4.48	0.297	302	11.6	2.30	0.107
48	1:1 PVA:TMM, 1.0, alum, 0.75, PAA, 1.0	24	62.5	156	0.399	5.21	0.092	5.90	0.211	304	17.7	2.76	0.007

Set No.	Additives, % based on fiber	Moist Strength Properties: Breaking Length km	SD	TEA kg/cm	SD	Et kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Oven Aging, hours at 105°C	Wet Breaking Length[d] km	SD	Wet Tensile Factor	In-plane moduli $E_{Young's}$	E_{Shear}	Out-of-Plane Modulus, E_Z	Fluorescence Size, s
14	Blank controls	1.89	0.740	2.24	0.211	157	14.3	2.77	0.200	1.00	--	0.108	0.004	1.00	4.442	1.747	0.364	Instantaneous
34	Blank controls	1.70	0.138	--	--	135	10.1	2.52	0.150	0.90	24	0.296	0.020	2.74	--	--	--	Instantaneous
35	Controls:alum, 0.75	1.76	0.018	2.12	0.129	138	13.2	2.73	0.134	0.93	--	0.128	0.014	1.19	4.325	1.671	0.365	Instantaneous
36	Controls:PVA[a], 1.0, alum, 0.75	1.82	0.134	1.84	0.272	143	9.1	2.44	0.182	0.96	--	0.123	0.008	1.14	4.573	1.828	0.354	Instantaneous
37	Controls:TMM[b] 0.5, alum, 0.75	1.70	0.173	2.07	0.263	148	9.9	2.92	0.131	0.90	--	0.399	0.014	3.69	--	--	--	--
38	Controls:PAA[c], 1.0	1.86	0.094	2.00	0.196	136	4.8	2.61	0.115	0.98	--	0.101	0.004	0.94	4.732	1.833	0.358	Instantaneous
39	Controls:PAA, 1.0	2.02	0.099	2.31	0.264	154	7.1	2.64	0.178	1.07	24	0.323	0.020	2.99	4.529	1.796	0.363	Instantaneous
40	1:1 PVA:TMM, 0.3, alum, 0.75	2.08	0.05	2.40	0.277	143	8.0	2.84	0.222	1.10	--	0.263	0.011	2.43	4.702	1.804	0.381	Instantaneous
41	1:1 PVA:TMM, 0.5, alum, 0.75	2.82	0.092	3.49	0.200	144	9.6	3.53	0.142	1.49	--	0.539	0.052	4.99	5.038	1.954	0.405	Instantaneous
42	1:1 PVA:TMM, 1.0, alum, 0.75	3.11	0.338	4.29	0.595	181	13.0	3.57	0.163	1.64	--	0.593	0.047	5.49	5.036	1.863	0.442	Instantaneous
43	1:1 PVA:TMM, 0.3, alum, 0.75, PAA, 1.0	2.36	0.087	2.89	0.195	162	10.0	3.04	0.098	1.25	--	0.303	0.019	2.80	4.705	1.908	0.380	Instantaneous
44	1:1 PVA:TMM, 0.5, alum, 0.75, PAA, 1.0	2.54	0.203	3.00	0.440	176	10.9	3.05	0.142	1.34	--	0.384	0.089	3.55	4.964	1.865	0.410	Instantaneous
45	1:1 PVA:TMM, 1.0, alum, 0.75, PAA, 1.0	2.95	0.286	3.72	0.631	174	9.8	3.32	0.309	1.56	--	0.589	0.025	5.45	5.037	1.961	0.430	Instantaneous
46	1:1 PVA:TMM, 0.3, alum, 0.75, PAA, 1.0	2.77	0.194	3.34	0.513	179	8.0	2.98	0.296	1.46	24	0.678	0.049	6.28	4.761	1.897	0.376	Instantaneous
47	1:1 PVA:TMM, 0.5, alum, 0.75, PAA, 1.0	2.74	0.351	3.34	0.819	169	8.6	3.05	0.321	1.45	24	0.759	0.061	7.03	4.865	1.945	0.390	Instantaneous
48	1:1 PVA:TMM, 1.0, alum, 0.75, PAA, 1.0	3.44	0.293	4.59	0.742	194	16.3	3.51	0.316	1.82	24	0.988	0.031	9.15	5.245	2.106	0.429	Instantaneous

[a]Polyvinyl alcohol.
[b]Trimethylol melamine.
[c]Polyacrylic acid: molecular weight 104,000.
[d]Soaked 24 hours in distilled water at room temperature.

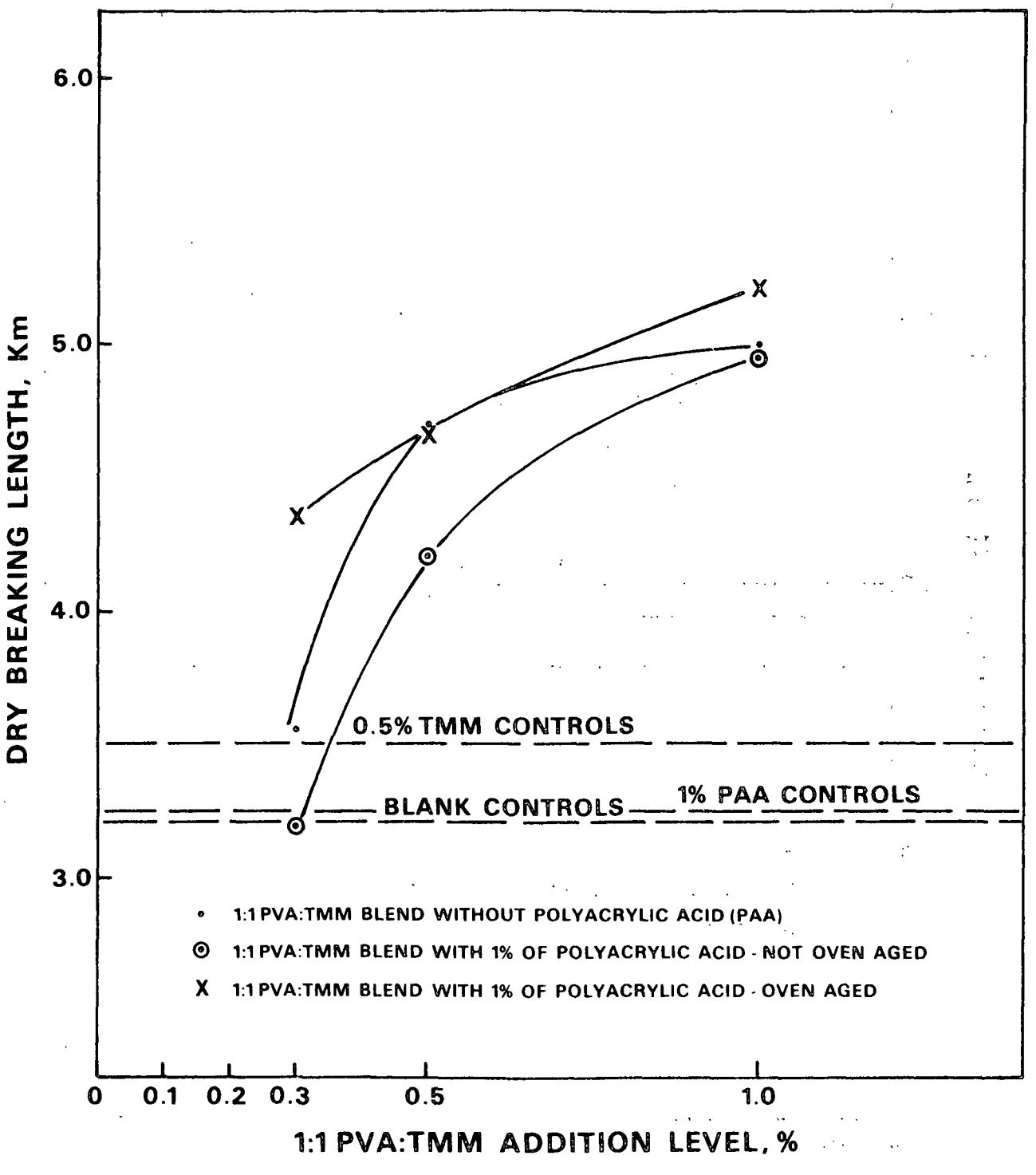


Figure 19. The effect of PVA:TMM addition level on dry tensile strength (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

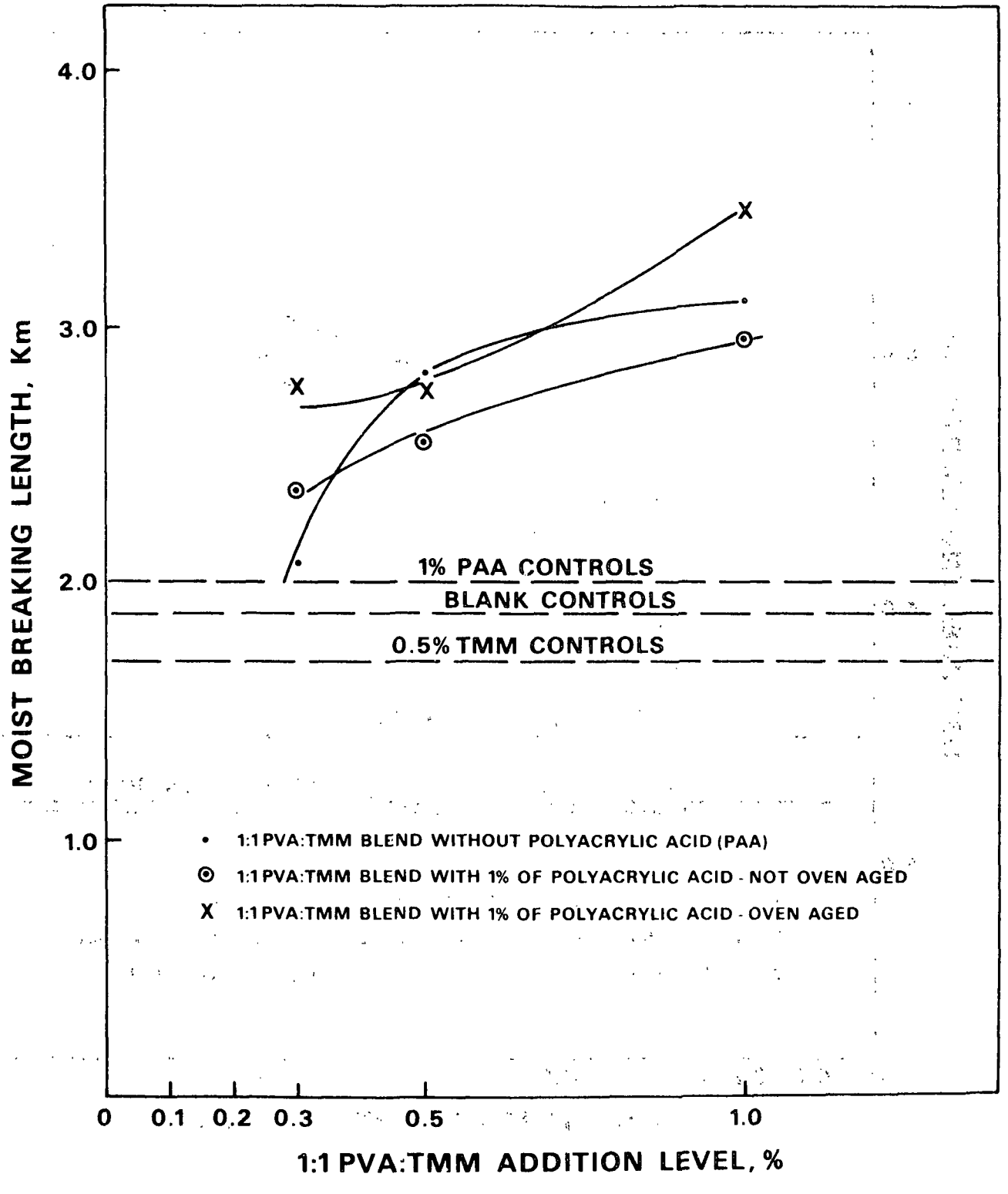


Figure 20. The effect of PVA:TMM addition level on moist tensile strength (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

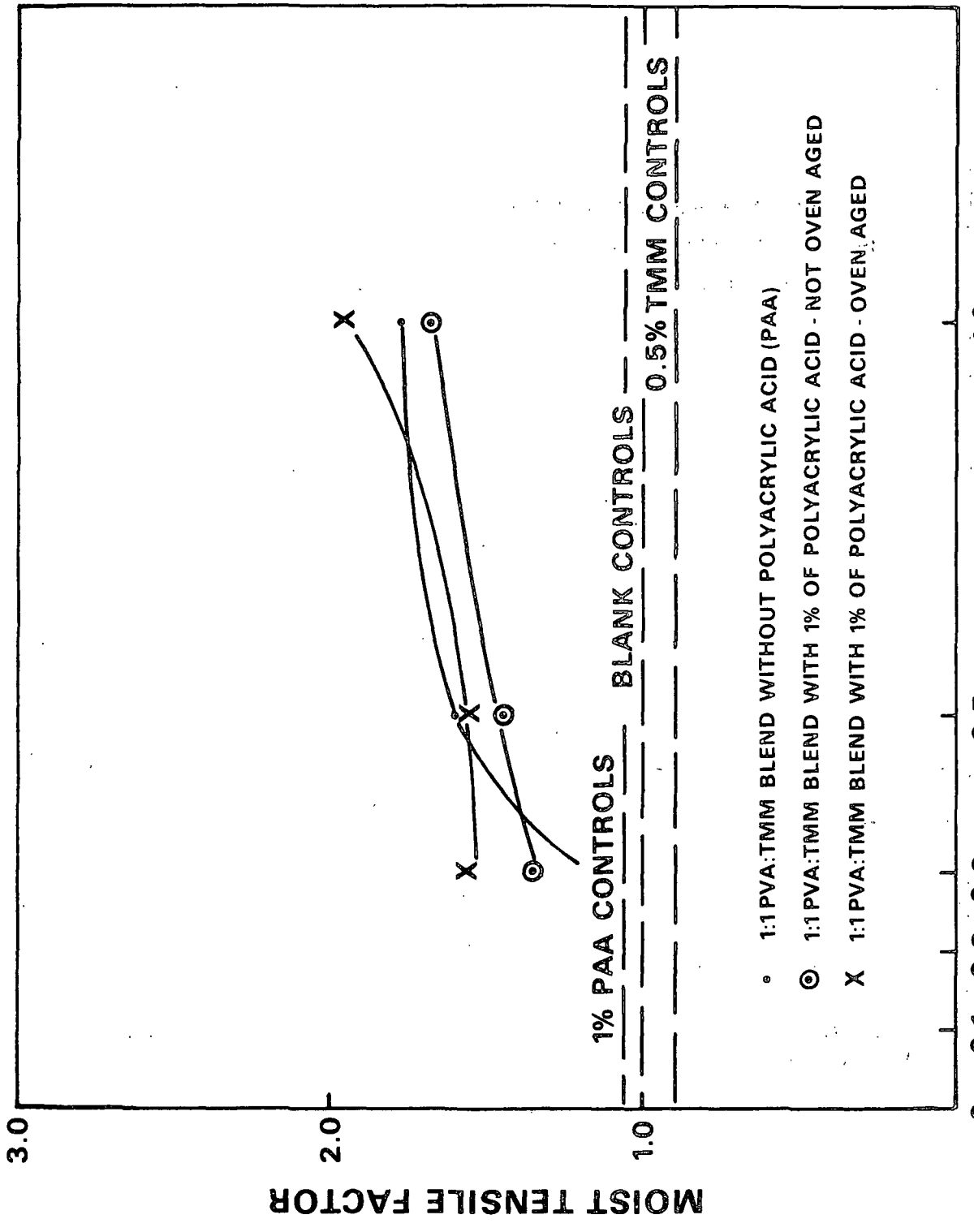


Figure 21. The effect of PVA:TMM addition level on moist tensile factor (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

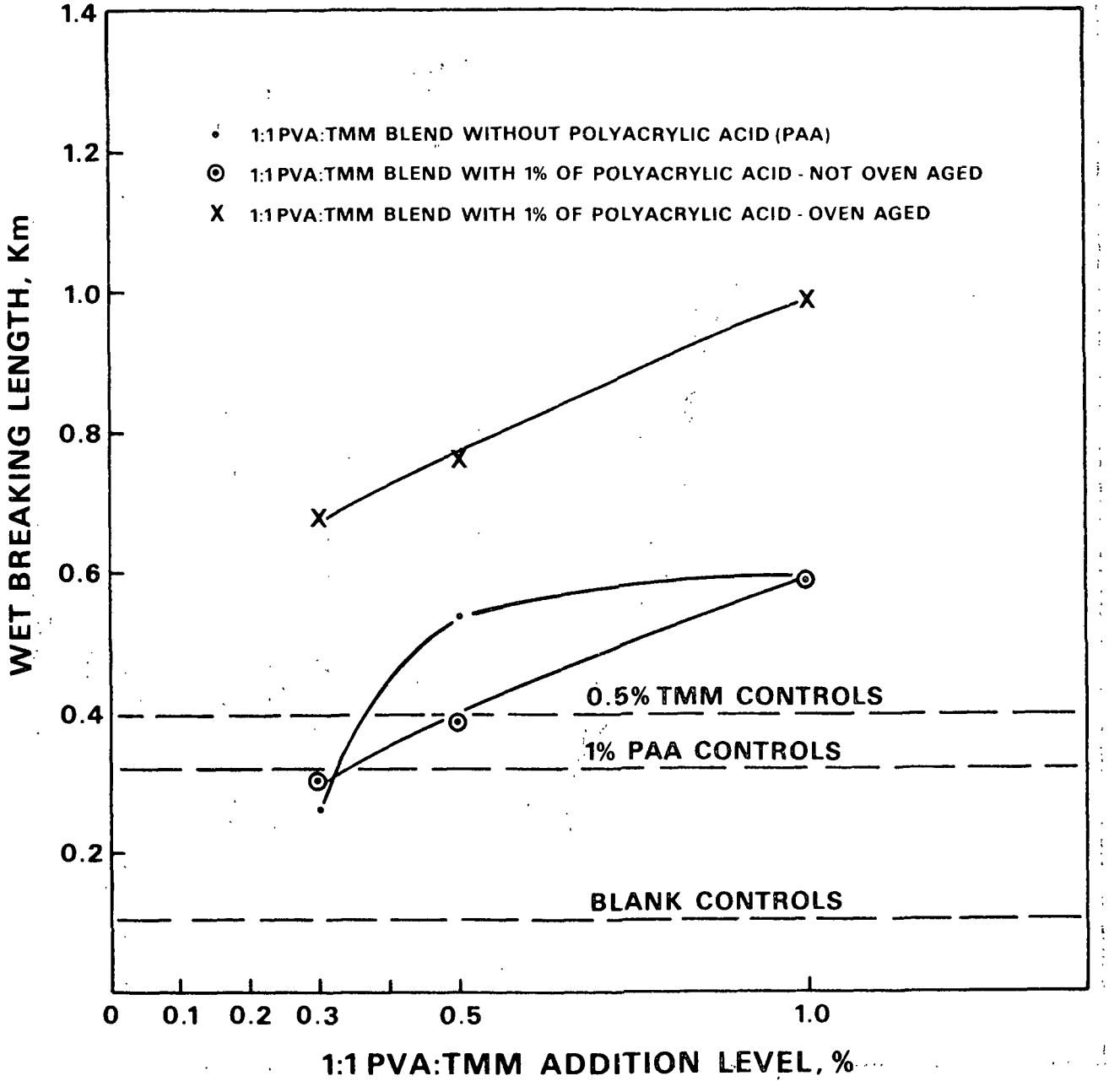


Figure 22. The effect of PVA:TMM addition level on wet tensile strength (24-hr soak) (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

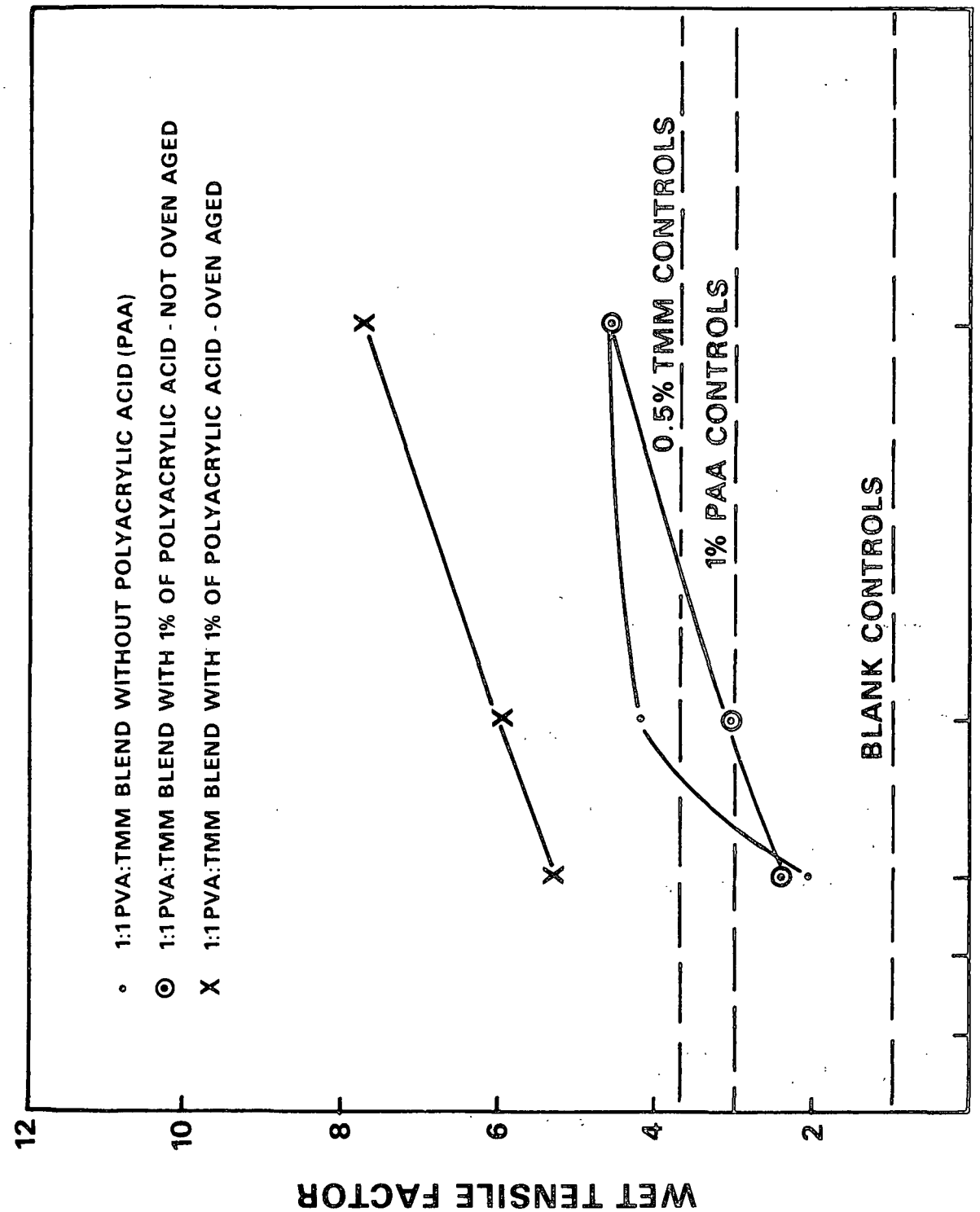


Figure 23. The effect of PVA:TMM addition level on wet tensile factor (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

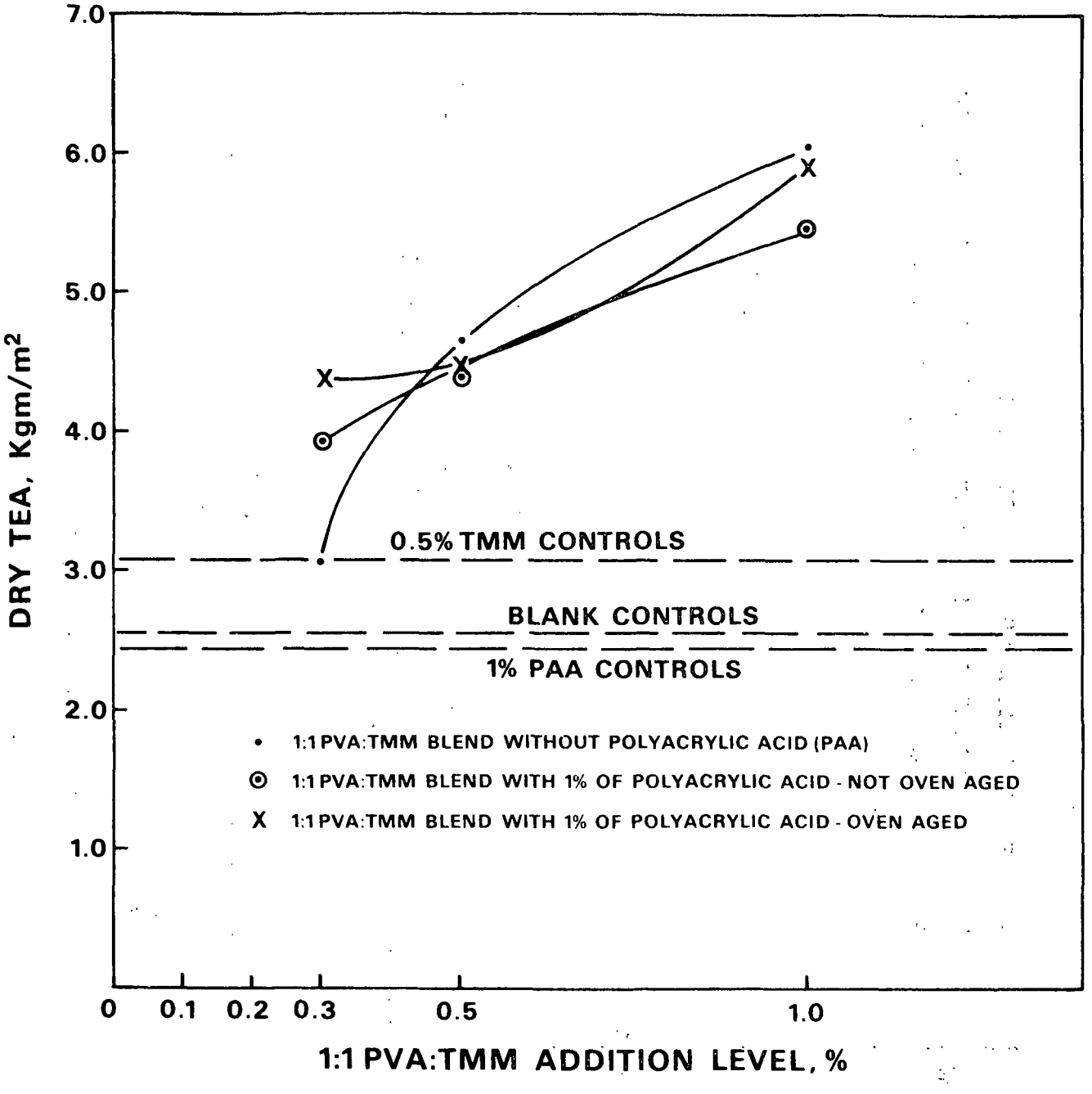


Figure 24. The effect of PVA:TMM addition level on tensile energy absorption (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

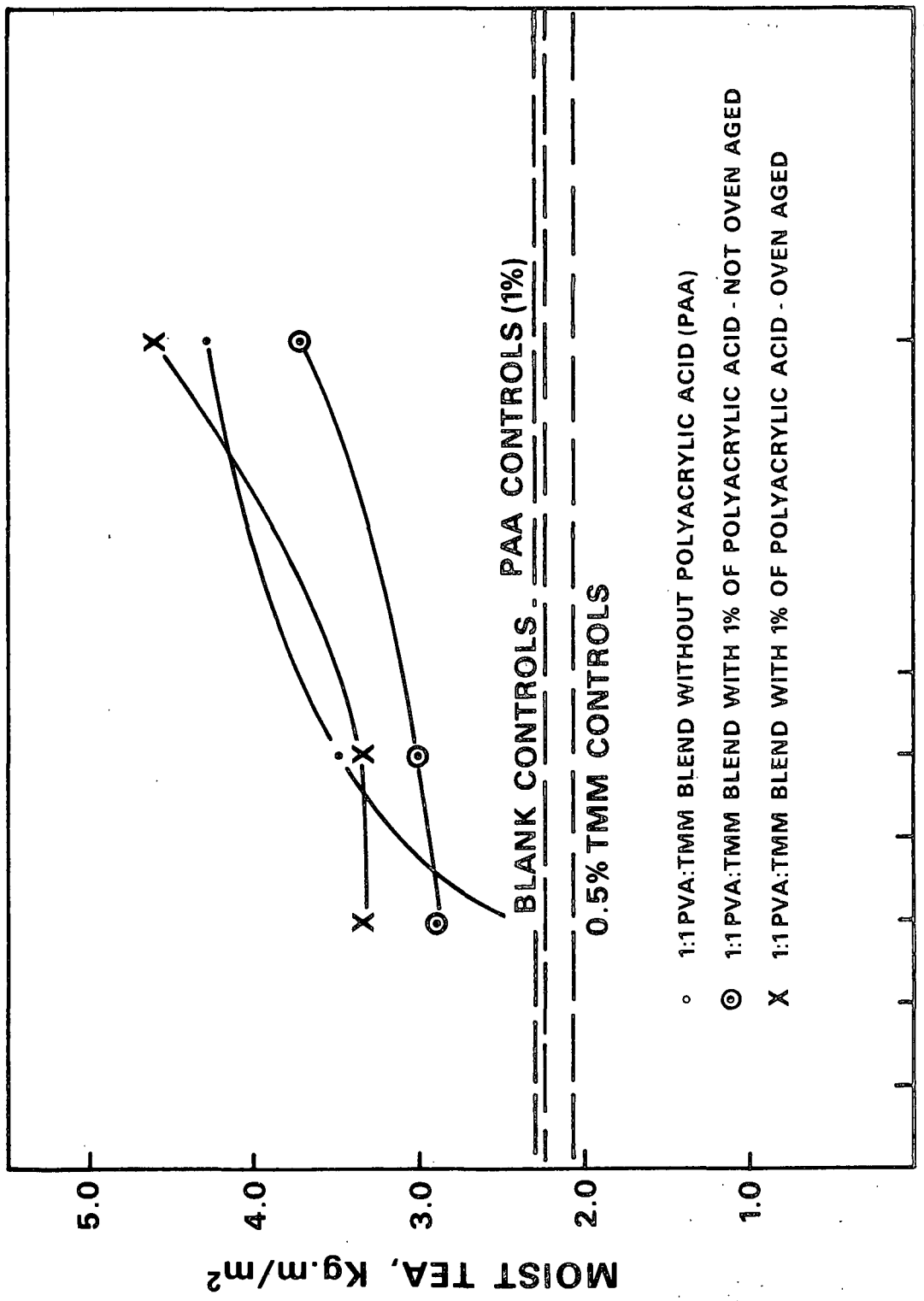


Figure 25. The effect of PVA:TMM addition level on moist tensile energy absorption (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

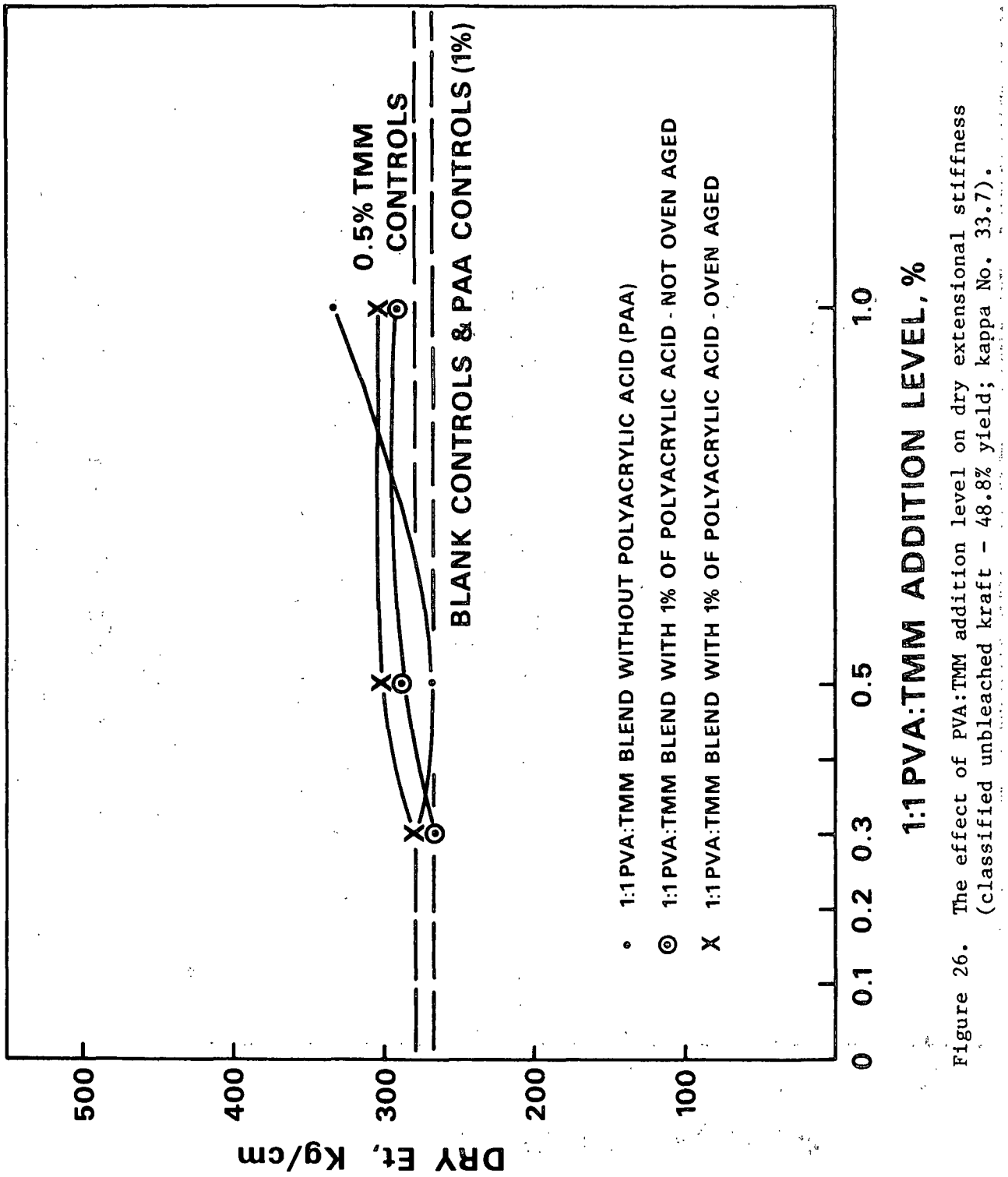


Figure 26. The effect of PVA:TMM addition level on dry extensional stiffness (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

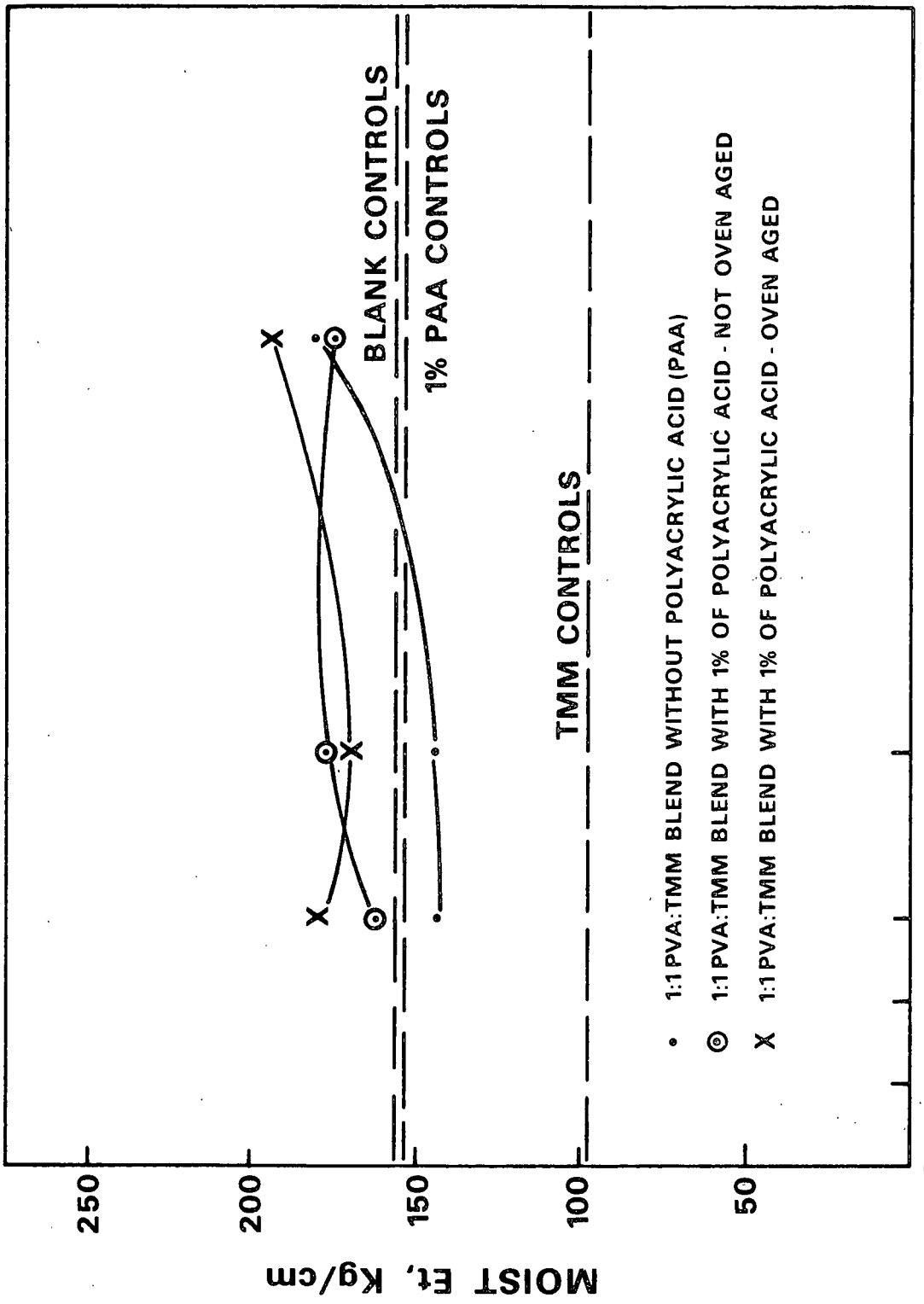


Figure 27. The effect of PVA:TMM addition level on moist extensional stiffness (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

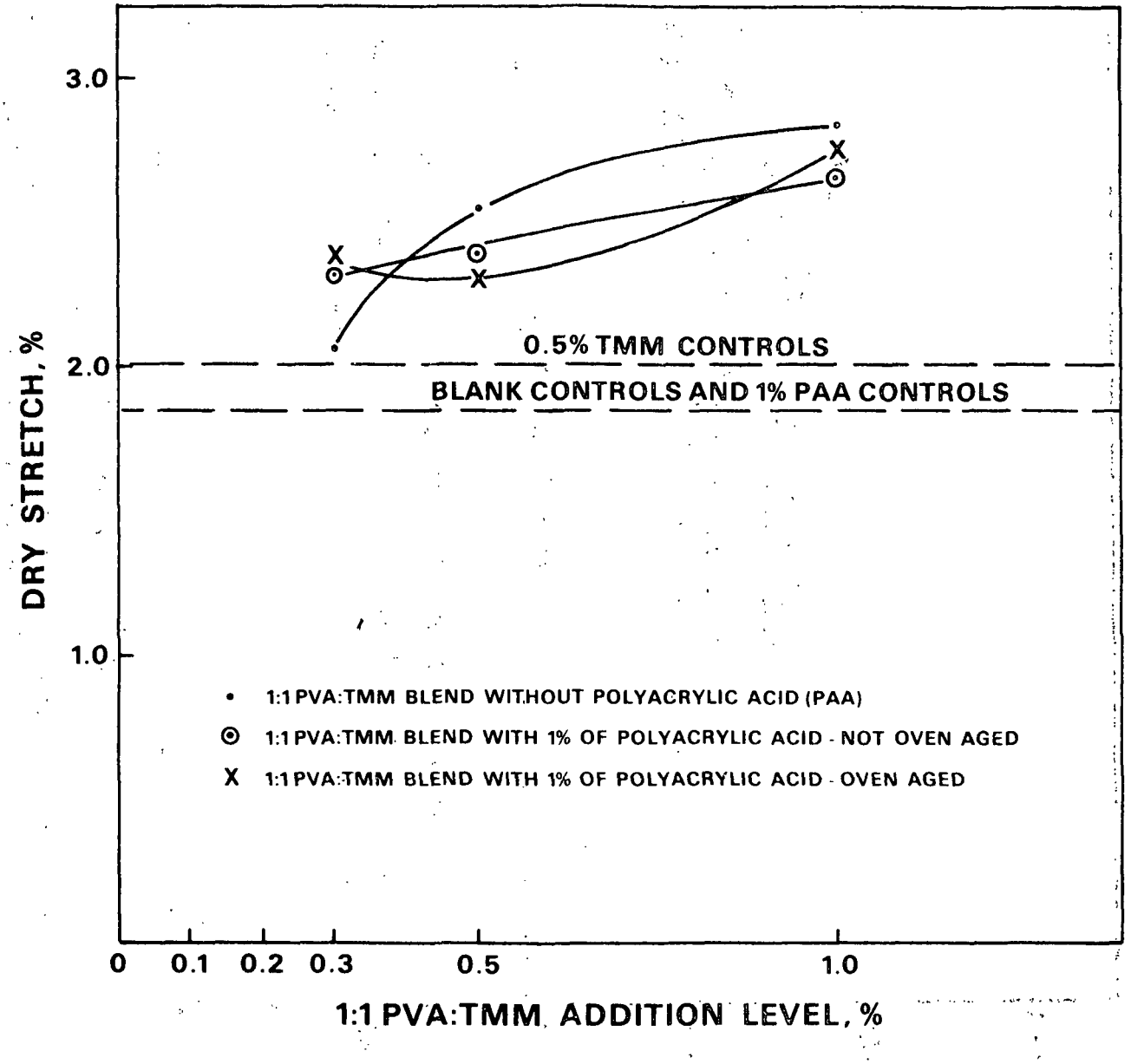


Figure 28. The effect of PVA:TMM addition level on dry stretch (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

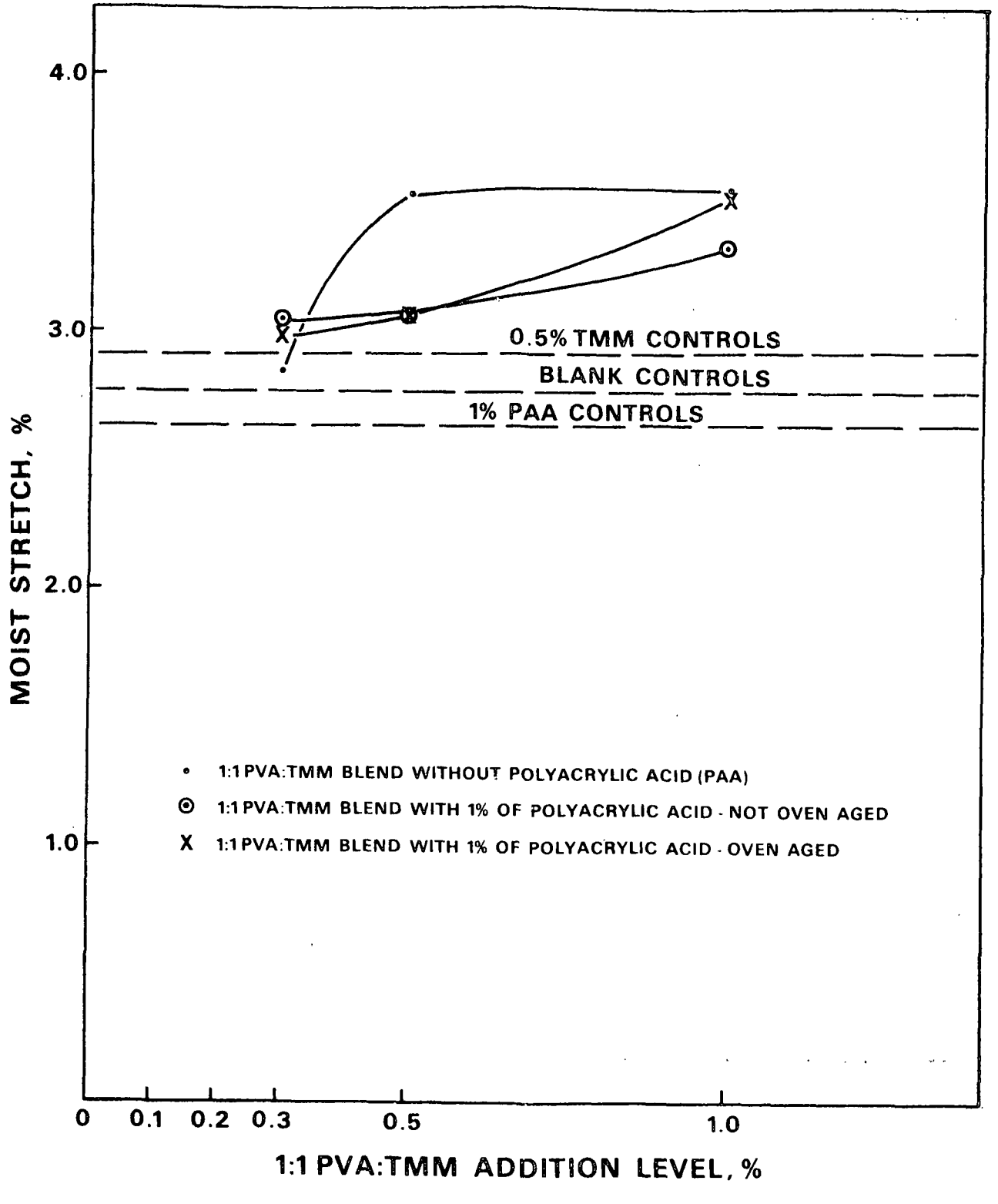


Figure 29. The effect of PVA:TMM addition level on moist stretch (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

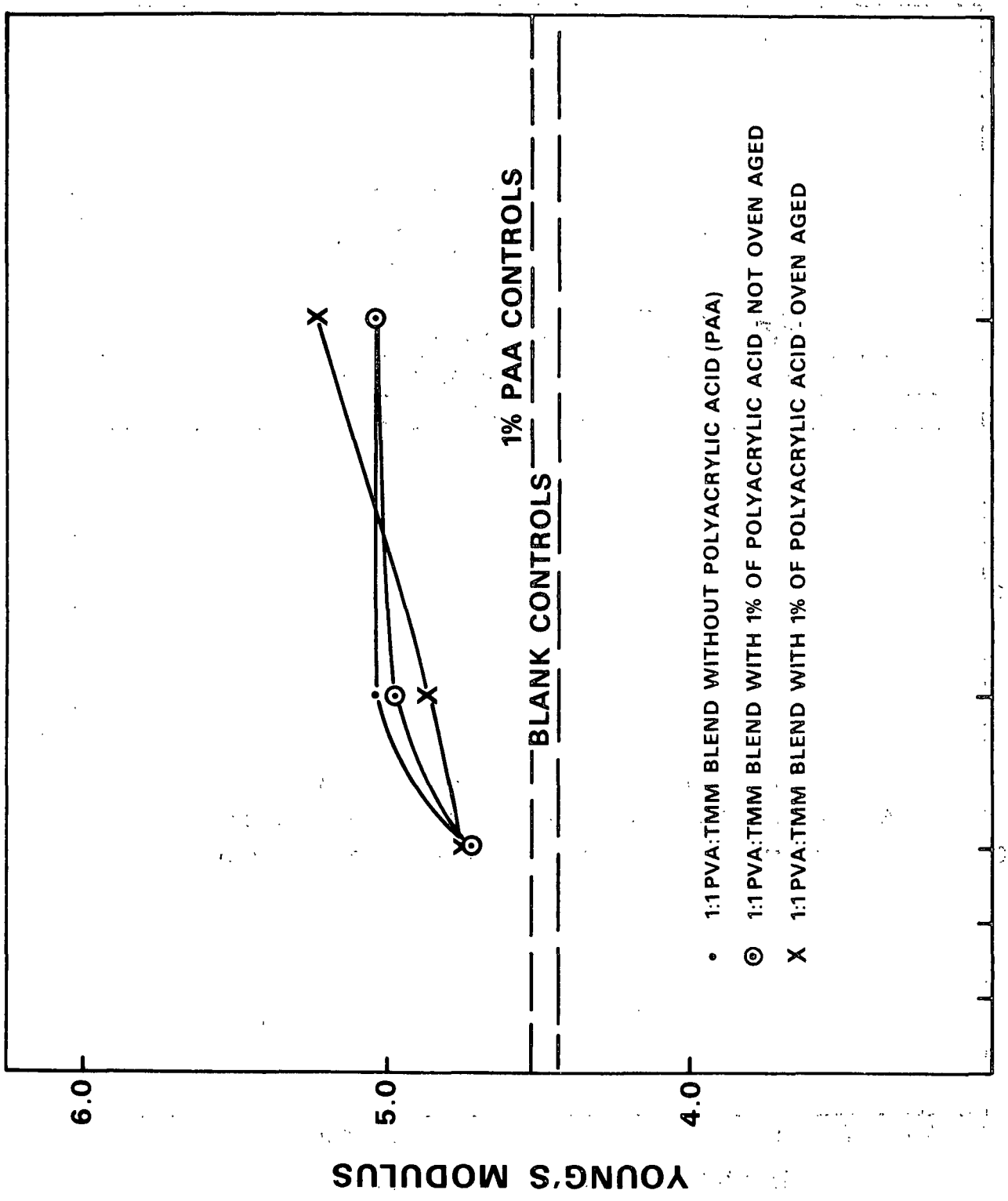


Figure 30. The effect of PVA:TMM addition level on Young's modulus (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

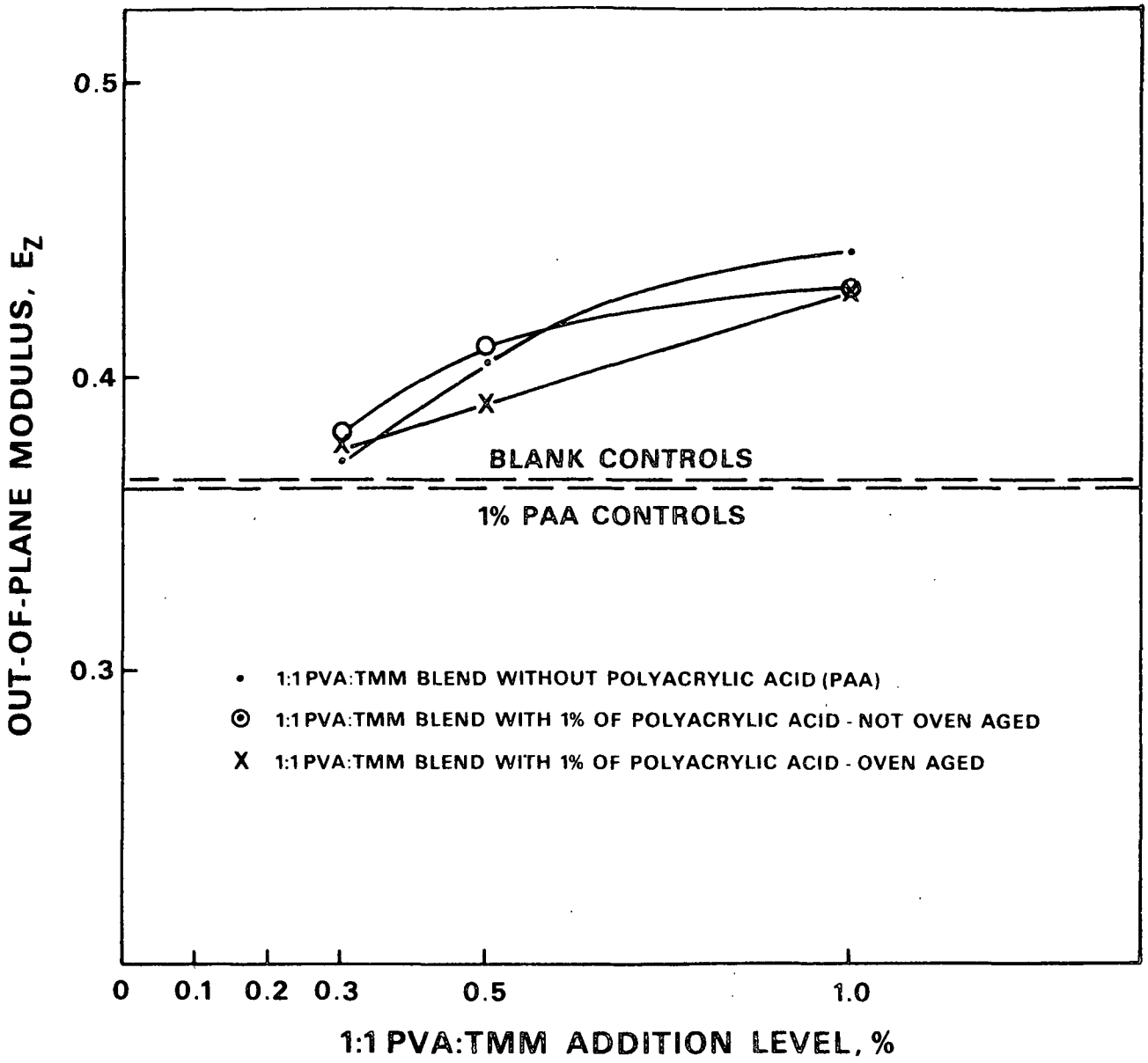


Figure 31. The effect of PVA:TMM addition level on out-of-plane modulus (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

Table 9. PVA/PAE combinations in classified softwood unbleached kraft pulp with and without polyacrylic acid (pulp - cook No. 1, 48.8% yield; kappa No. 33.7).

Set No.	Additives, % based on fiber	Oven Aging, hours at 105°C	Basis Wt., g/m²	Thickness µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD
14	Blank controls	--	63.1	161	0.390	3.22	0.145	2.56	0.382	261	11.3	1.84	0.177
34	Blank controls	24	63.6	162	0.391	3.41	0.261	--	--	240	17.2	1.98	0.200
15	Controls; PAE[a], 0.5	--	63.5	164	0.387	4.01	0.645	3.89	1.270	287	25.2	2.23	0.408
49	1:1 PVA[b]:PAE, 0.3	--	63.6	160	0.398	4.04	0.314	3.74	0.644	274	21.5	2.10	0.061
50	1:1 PVA:PAE, 0.5	--	62.2	162	0.383	4.28	0.320	4.03	0.740	256	13.9	2.30	0.248
51	1:1 PVA:PAE, 1.0	--	61.8	164	0.377	3.99	0.342	3.48	0.939	254	9.1	2.13	0.400
52	1:1 PVA:PAE, 0.3; PAA[c], 1.0	--	60.4	152	0.398	4.40	0.261	4.29	0.715	290	14.1	2.36	0.272
53	1:1 PVA:PAE, 0.5; PAA, 1.0	--	62.4	155	0.402	4.85	0.509	5.26	0.125	329	12.0	2.49	0.360
54	1:1 PVA:PAE, 1.0; PAA, 1.0	--	63.6	146	0.435	5.94	0.396	7.91	0.909	367	32.4	3.14	0.201
55	1:1 PVA:PAE, 0.3; PAA, 1.0	24	56.6	148	0.383	4.52	0.410	3.76	0.933	287	5.4	2.18	0.366
56	1:1 PVA:PAE, 0.5, PAA, 1.0	24	62.3	153	0.406	5.44	0.210	5.84	0.431	337	19.4	2.57	0.119
57	1:1 PVA:PAE, 1.0, PAA, 1.0	24	66.0	155	0.426	6.38	0.483	7.98	1.187	396	17.2	2.82	0.214
58	PAE, 0.5, PAA, 1.0	--	62.3	152	0.410	4.84	0.462	5.22	1.450	322	23.9	2.52	0.474

Set No.	Additives, % based on fiber	Moist Strength Properties (~16% Moisture): Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Oven Aging, hours, at 105°C	Wet Breaking Length[d] km	SD	Wet Tensile Factor	In-Plane Moduli: $E_{Young's}$	E_{shear}	Out-of-plane Modulus, E_z	Fluorescence Size, s
14	Blank controls	1.89	0.740	2.24	0.211	157	14.3	2.77	0.200	1.00	--	0.108	0.004	1.0	4.442	1.747	0.364	Instantaneous
34	Blank controls	1.70	0.138	--	--	135	10.1	2.52	0.150	0.90	24	0.296	0.020	2.74	--	--	--	Instantaneous
15	Controls; PAE[a], 0.5	2.37	0.161	3.37	0.351	102	16.2	3.72	0.267	1.25	--	0.900	0.078	8.33	--	--	--	Instantaneous
49	1:1 PVA[b]:PAE, 0.3	2.82	0.113	3.87	0.341	173	12.2	3.49	0.149	1.49	--	0.697	0.043	6.45	5.102	1.951	0.404	Instantaneous
50	1:1 PVA:PAE, 0.5	2.49	0.190	2.86	0.379	147	16.4	3.02	0.235	1.32	--	0.761	0.069	7.05	4.962	1.941	0.417	Instantaneous
51	1:1 PVA:PAE, 1.0	2.45	0.260	2.93	0.546	138	7.0	3.16	0.272	1.30	--	0.919	0.037	8.51	4.899	1.824	0.417	Instantaneous
52	1:1 PVA:PAE, 0.3; PAA[c], 1.0	2.67	0.129	3.18	0.276	165	8.4	3.17	0.104	1.41	--	0.753	0.099	6.97	5.205	1.909	0.415	Instantaneous
53	1:1 PVA:PAE, 0.5; PAA, 1.0	3.11	0.290	4.13	0.675	182	17.8	3.44	0.282	1.64	--	0.816	0.065	7.55	5.230	2.006	0.421	Instantaneous
54	1:1 PVA:PAE, 1.0; PAA, 1.0	3.64	0.182	5.47	0.362	178	11.7	4.07	0.145	1.92	--	1.12	0.051	9.26	5.510	2.103	0.472	Instantaneous
55	1:1 PVA:PAE, 0.3; PAA, 1.0	2.83	0.199	2.92	0.223	149	9.0	3.02	0.143	1.50	24	0.941	0.087	8.71	4.999	1.968	0.408	Instantaneous
56	1:1 PVA:PAE, 0.5, PAA, 1.0	3.65	0.122	5.06	0.141	192	10.0	3.71	0.080	1.93	24	1.270	0.047	11.76	5.535	2.11	0.414	Instantaneous
57	1:1 PVA:PAE, 1.0, PAA, 1.0	4.35	0.364	6.97	1.007	215	13.1	4.16	0.251	2.30	24	1.620	0.081	15.00	5.941	2.268	0.465	Instantaneous
58	PAE, 0.5, PAA, 1.0	2.60	0.434	3.96	1.14	104	26.3	4.10	0.527	1.38	--	1.17	0.048	10.83	--	--	--	Instantaneous

[a]Polyaminde polyamine epichlorohydrin.
[b]Polyvinyl alcohol.
[c]Polyacrylic acid; molecular weight 104,000.
[d]Soaked 24 hours at room temperature.

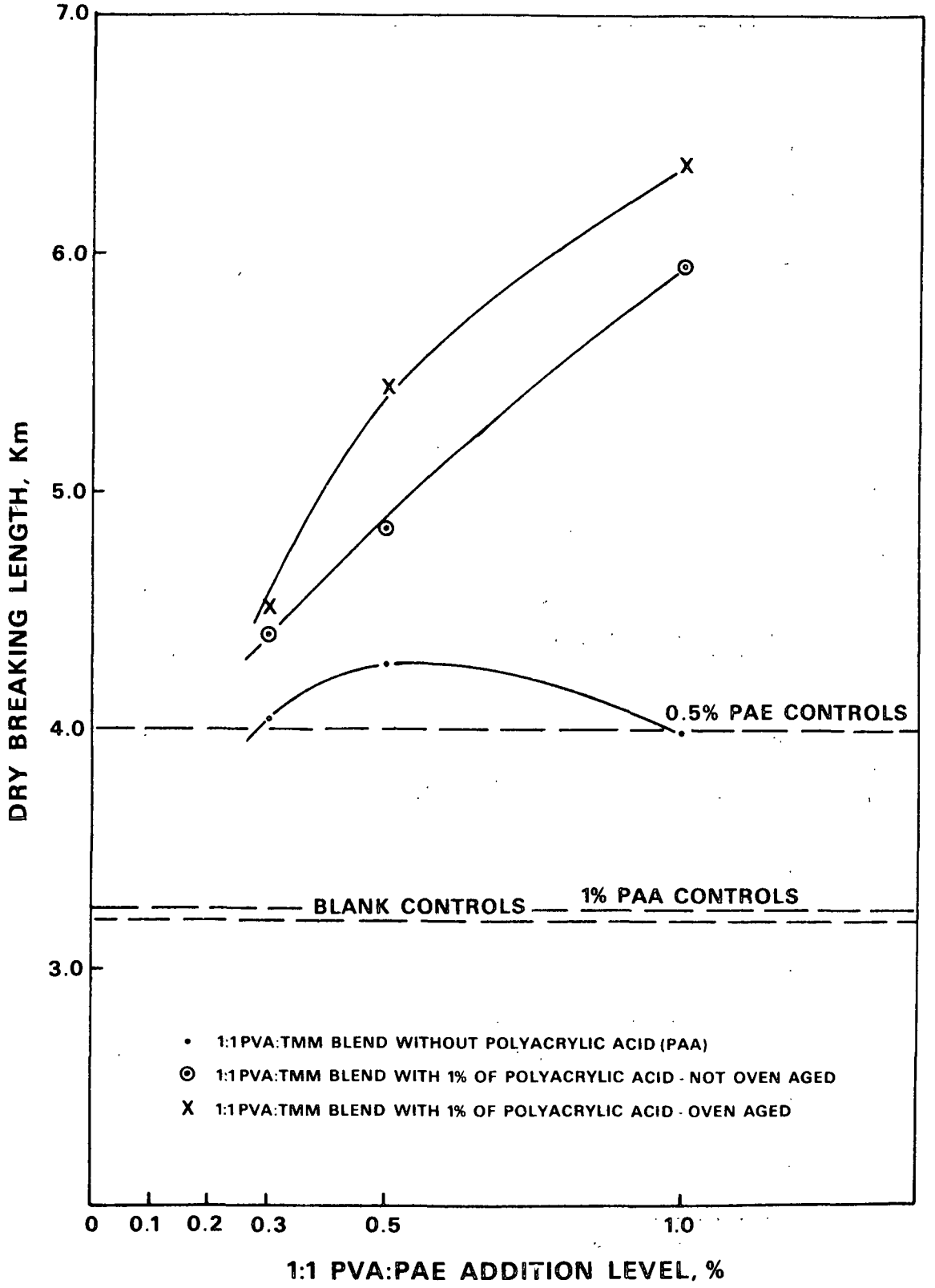


Figure 32. The effect of PVA:PAE addition level on dry tensile strength (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

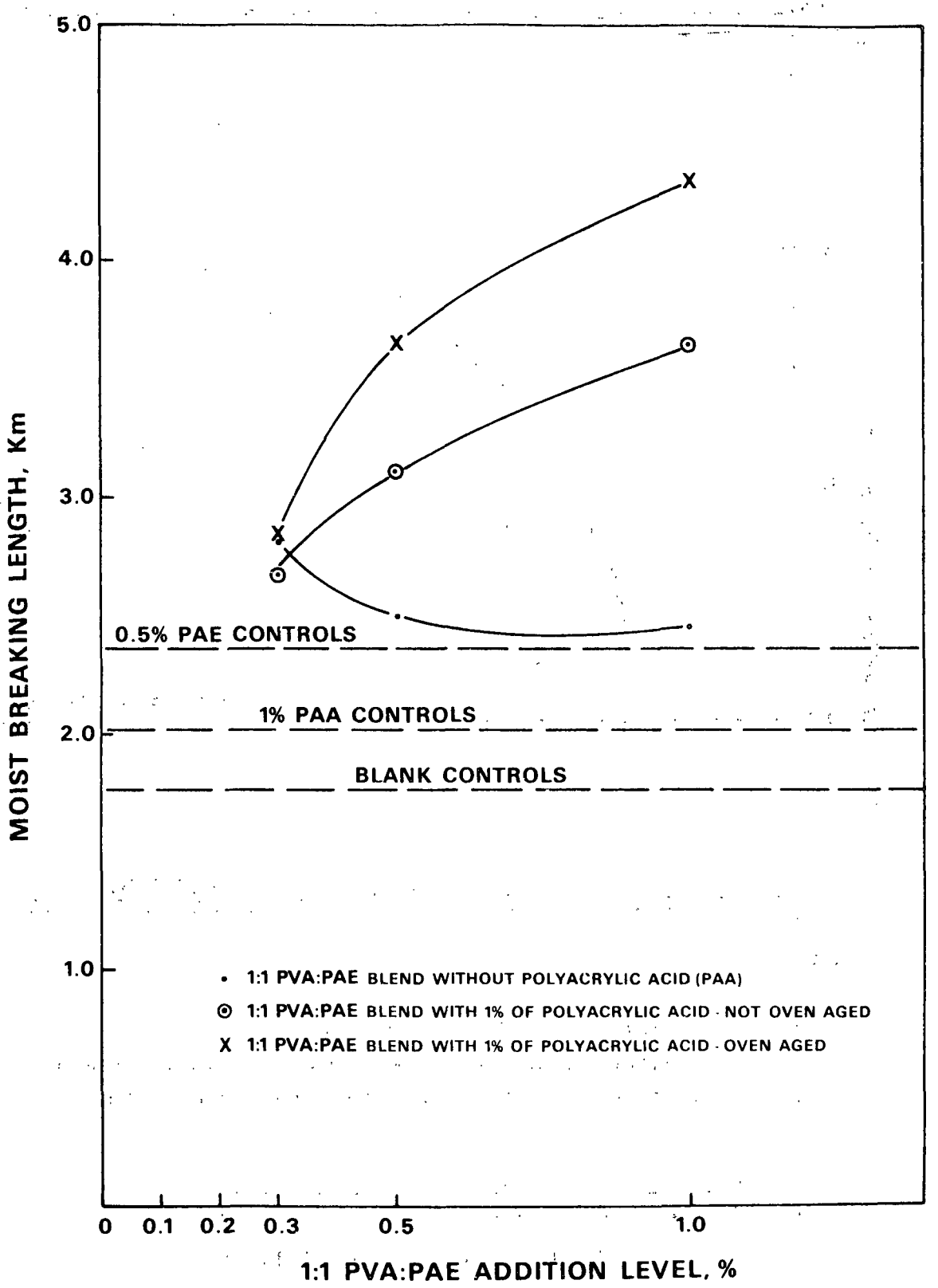


Figure 33. The effect of PVA:PAE addition level on moist tensile strength (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

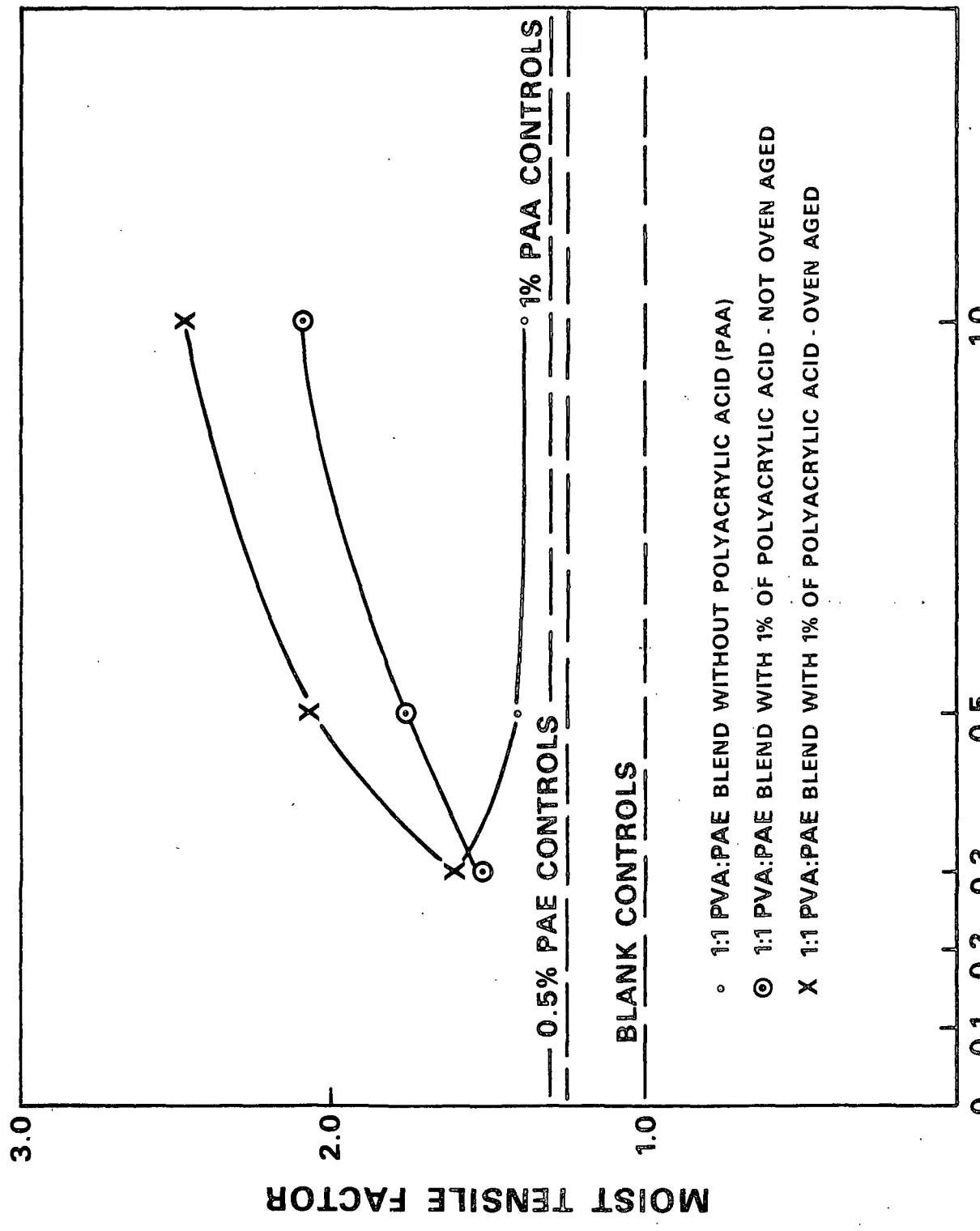


Figure 34. The effect of PVA:PAE addition level on moist tensile factor (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

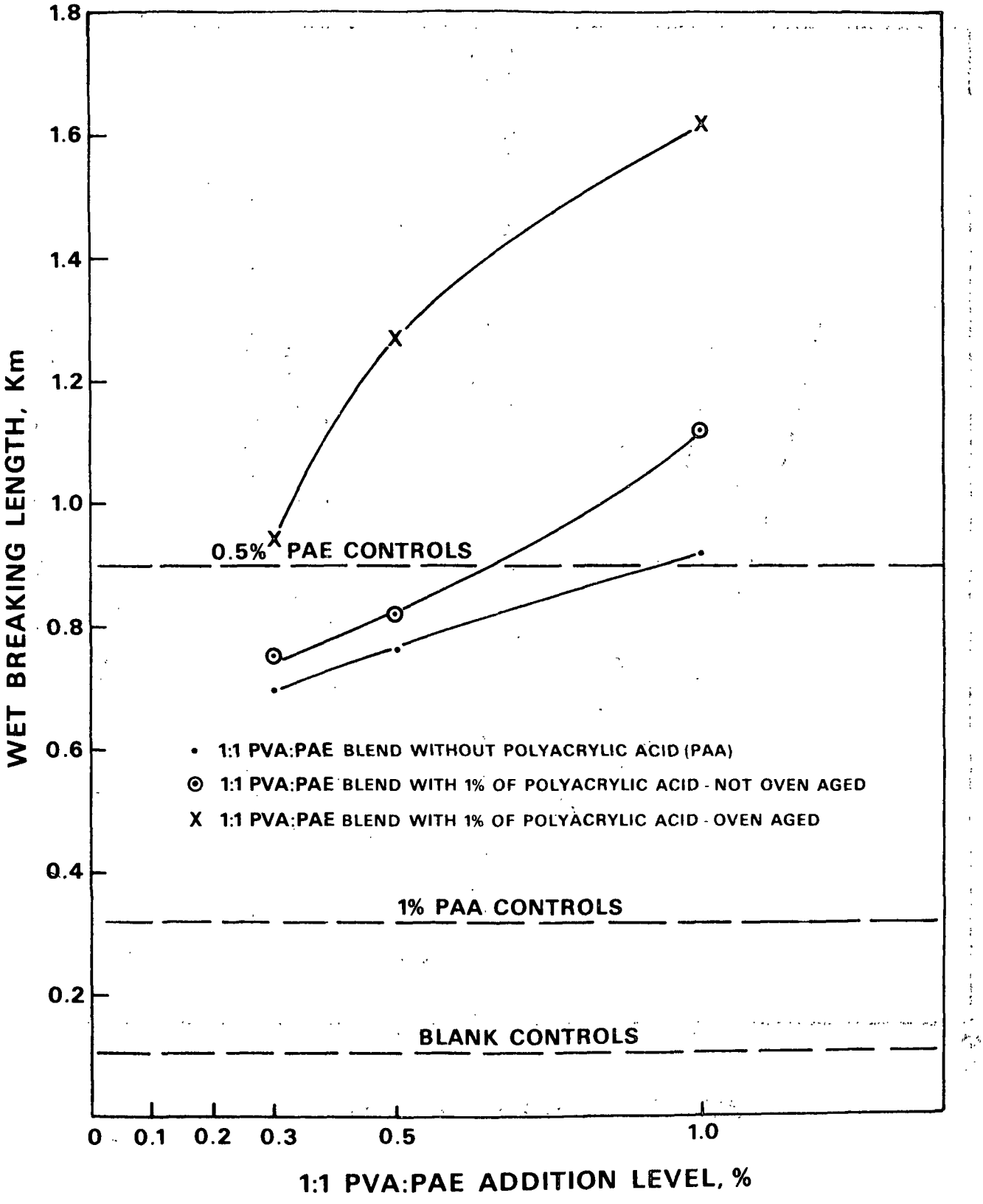


Figure 35. The effect of PVA:PAE addition level on wet tensile strength (24-hour soak) (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

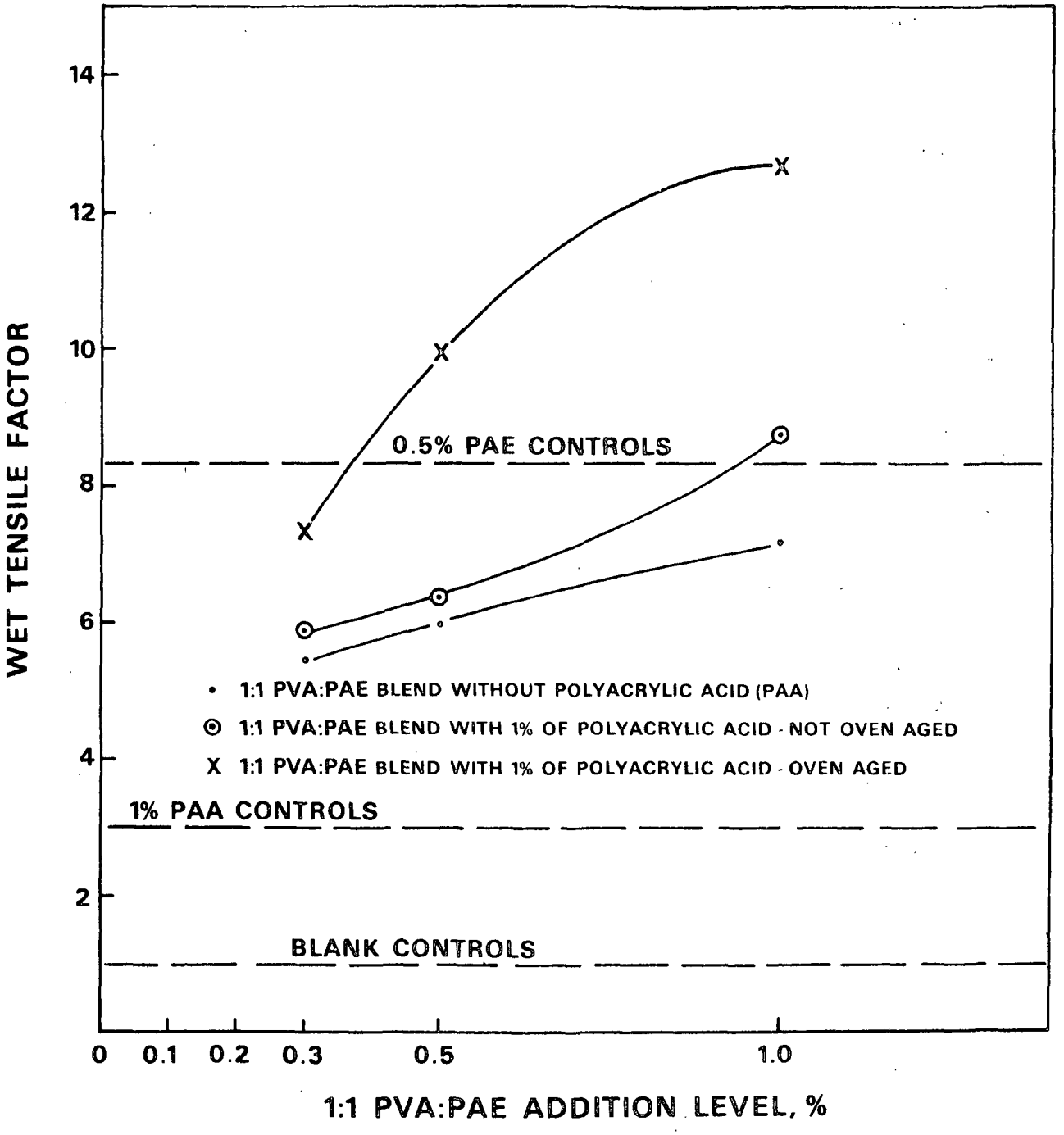


Figure 36. The effect of PVA:PAE addition level on wet tensile factor (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

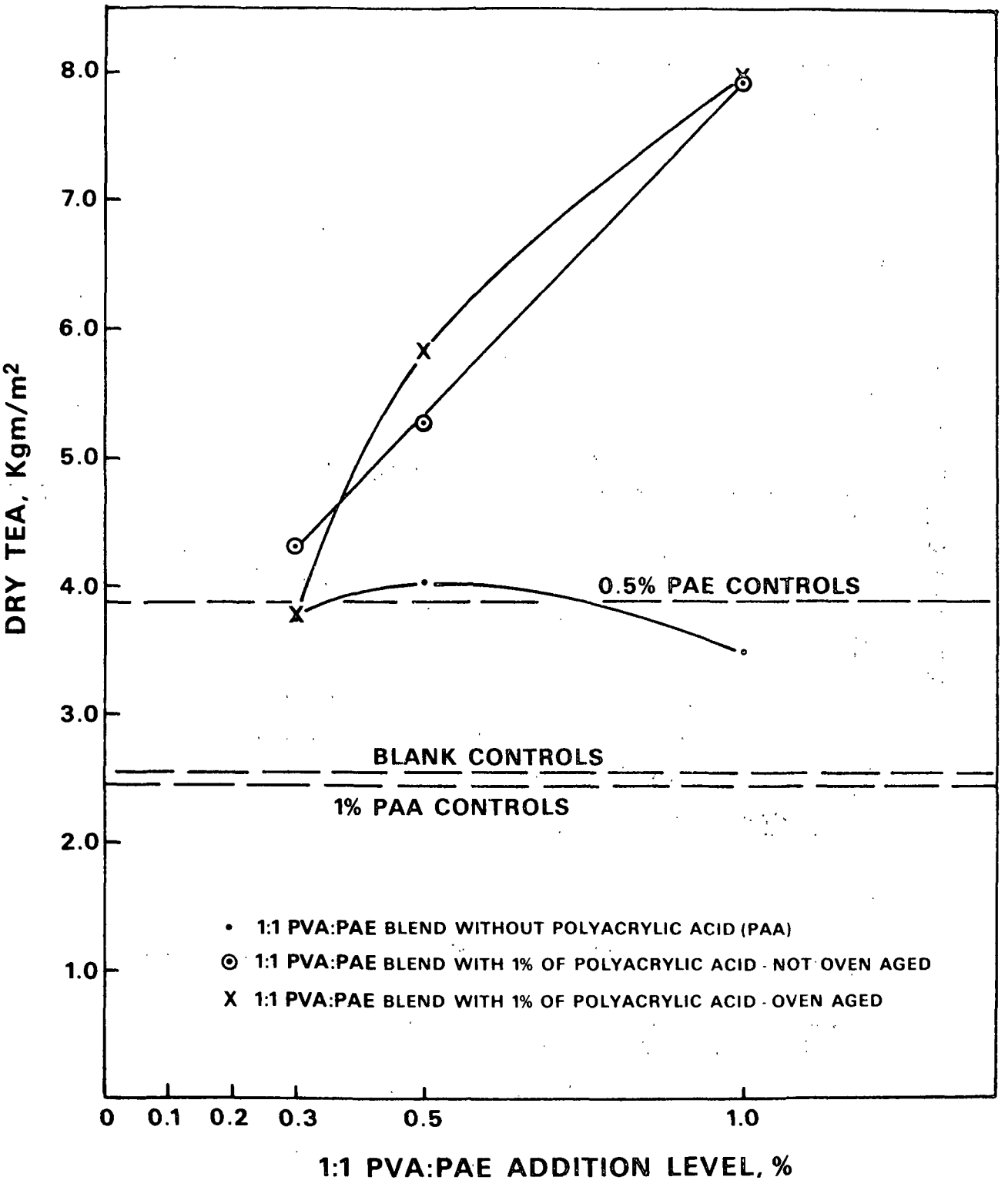


Figure 37. The effect of PVA:PAE addition level on tensile energy absorption (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

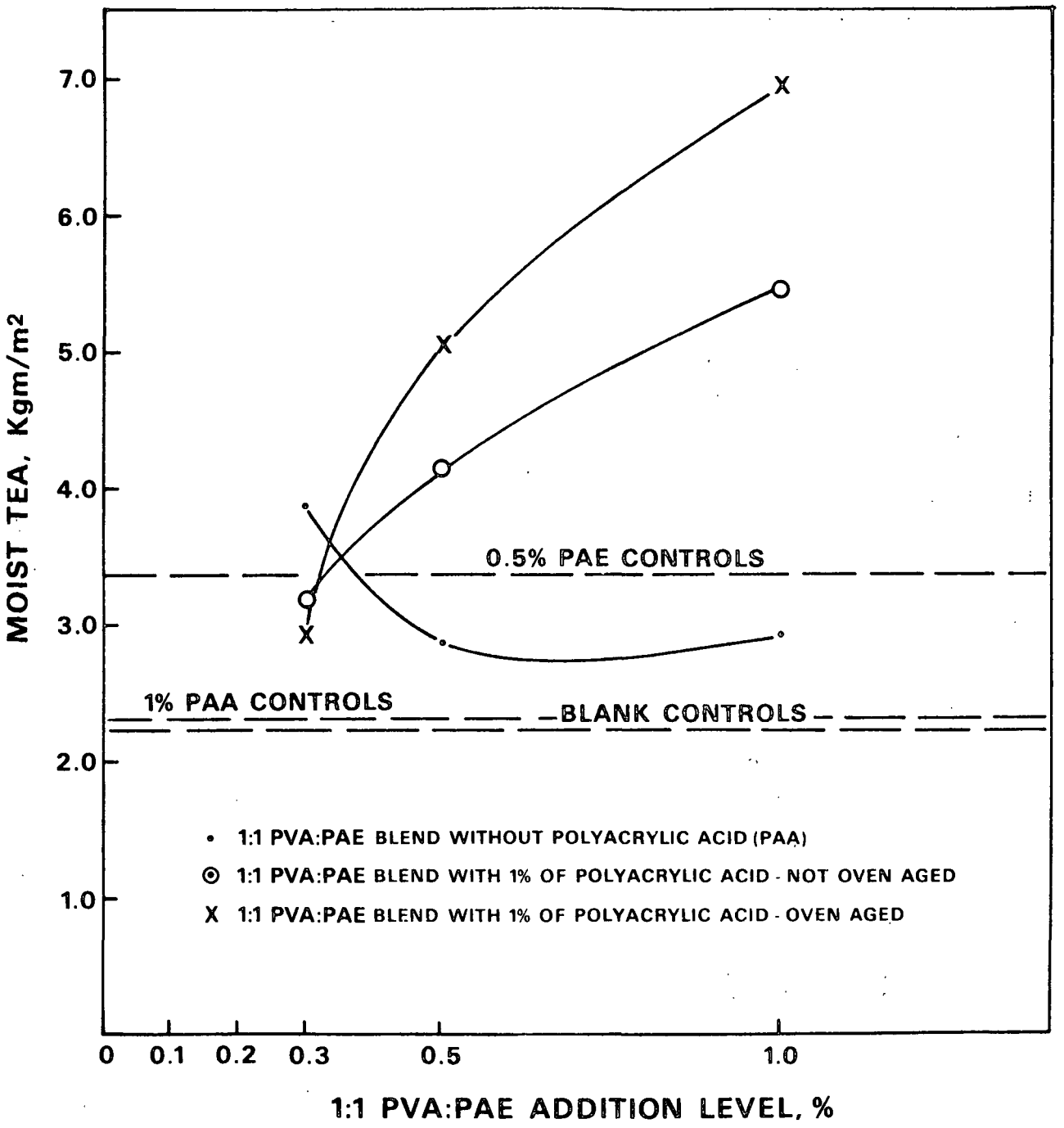


Figure 38. The effect of PVA:PAE addition level on moist tensile energy absorption (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

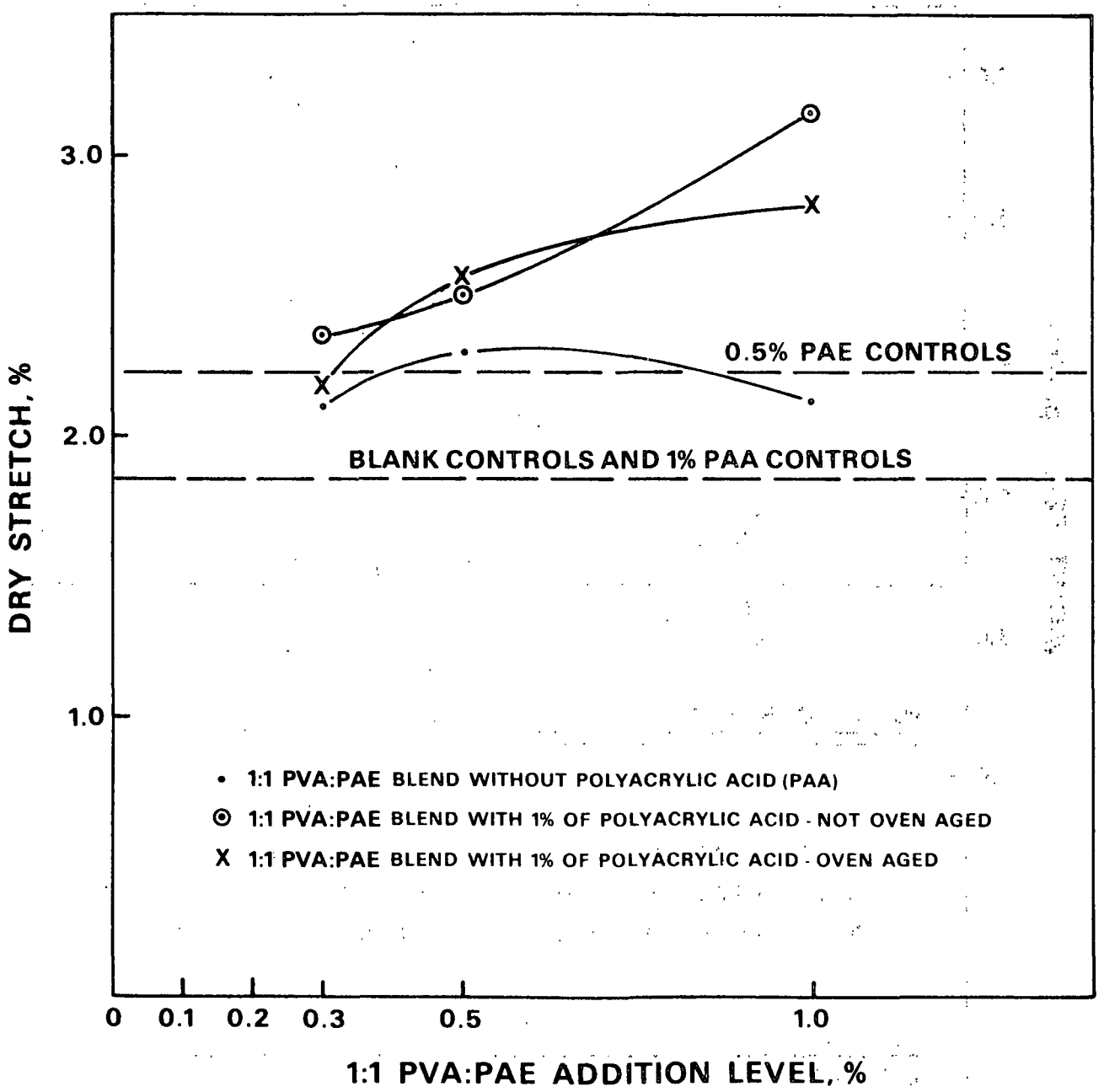


Figure 39. The effect of PVA:PAE addition level on dry stretch (classified unbleached kraft - 48.8% yield, kappa No. 33.7).

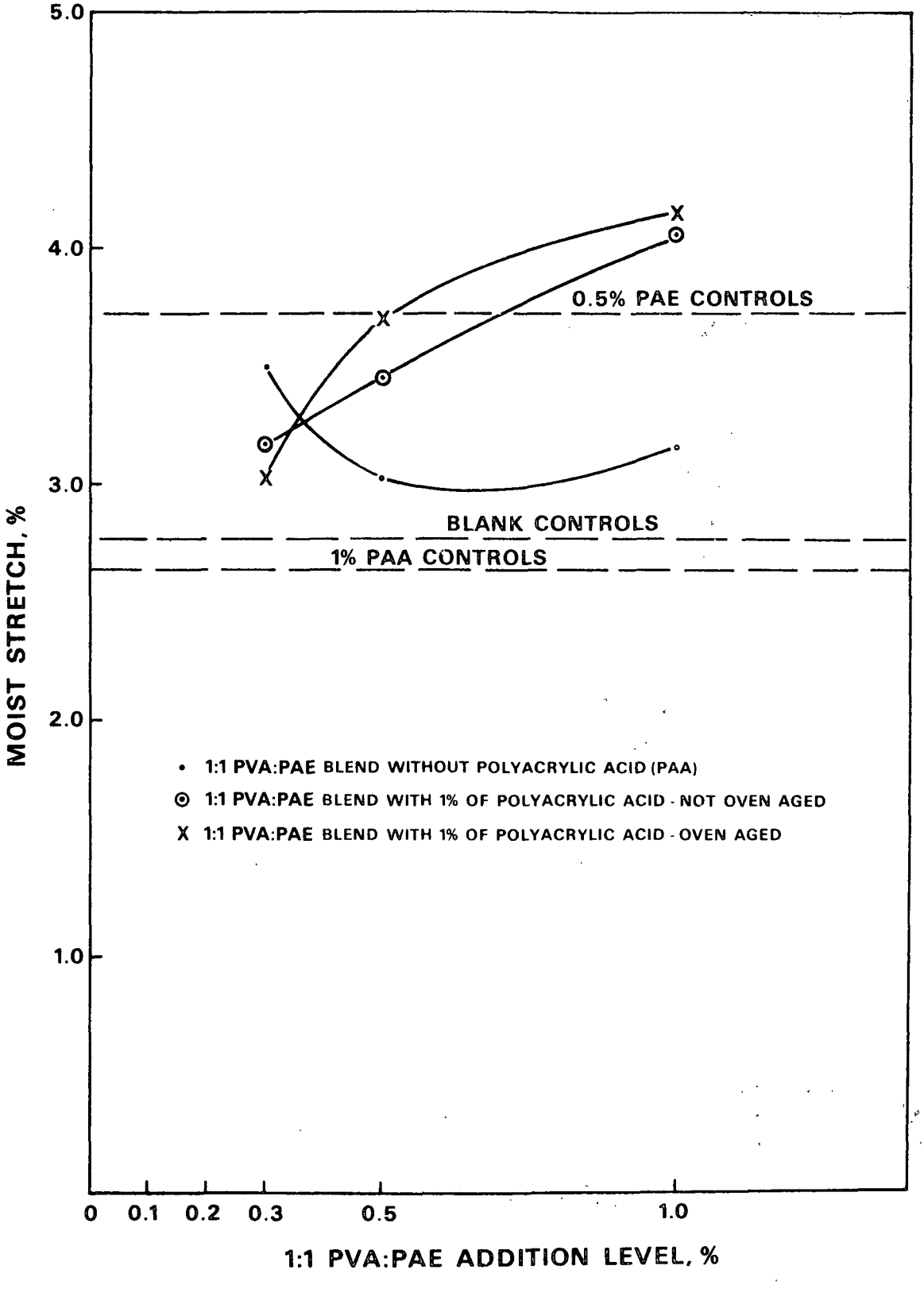


Figure 40. The effect of PVA:PAE addition level on moist stretch (classified unbleached kraft - 48.8% yield; kappa No. 33.7)

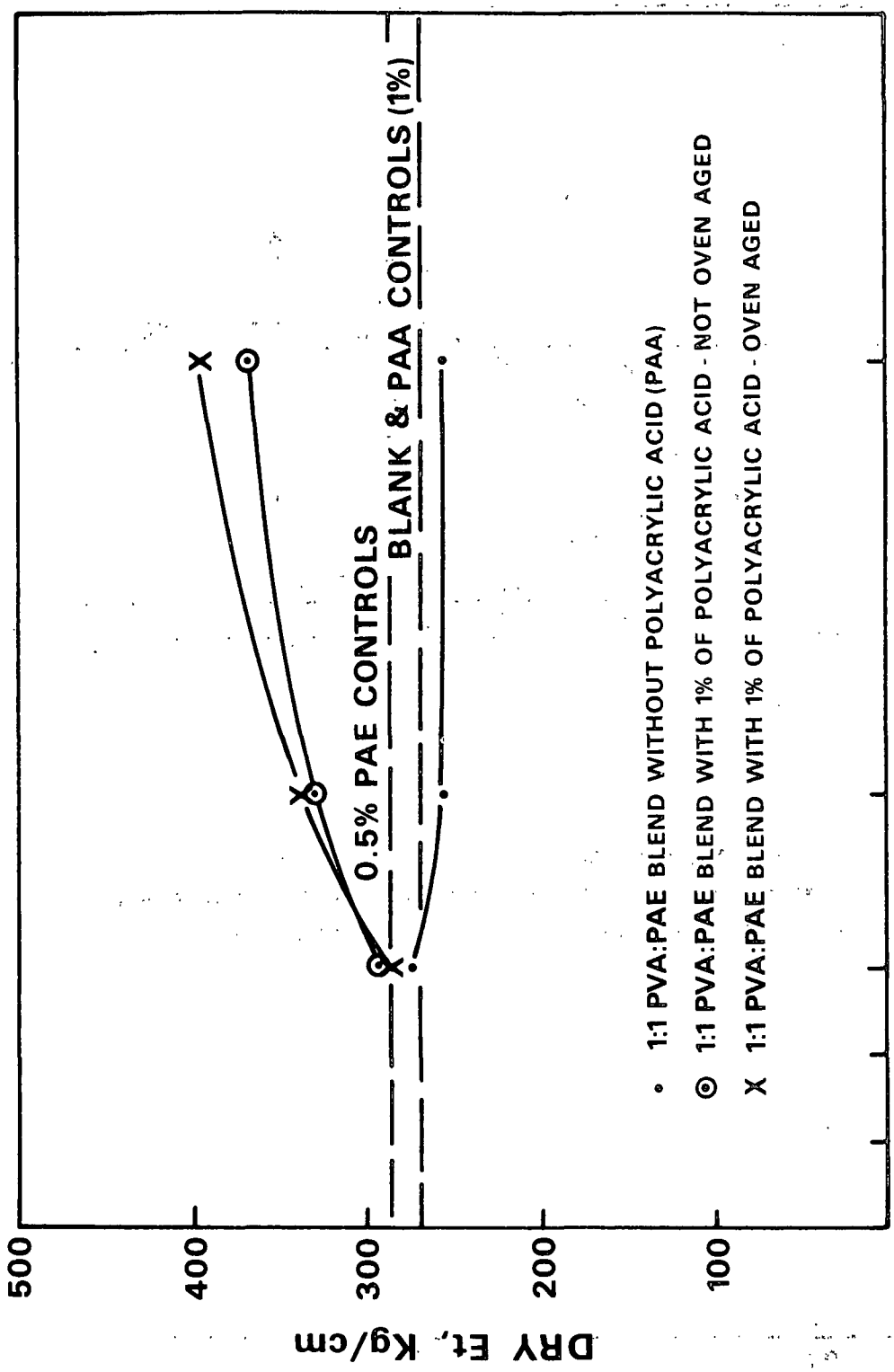


Figure 41. The effect of PVA:PAE addition level on dry extensional stiffness (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

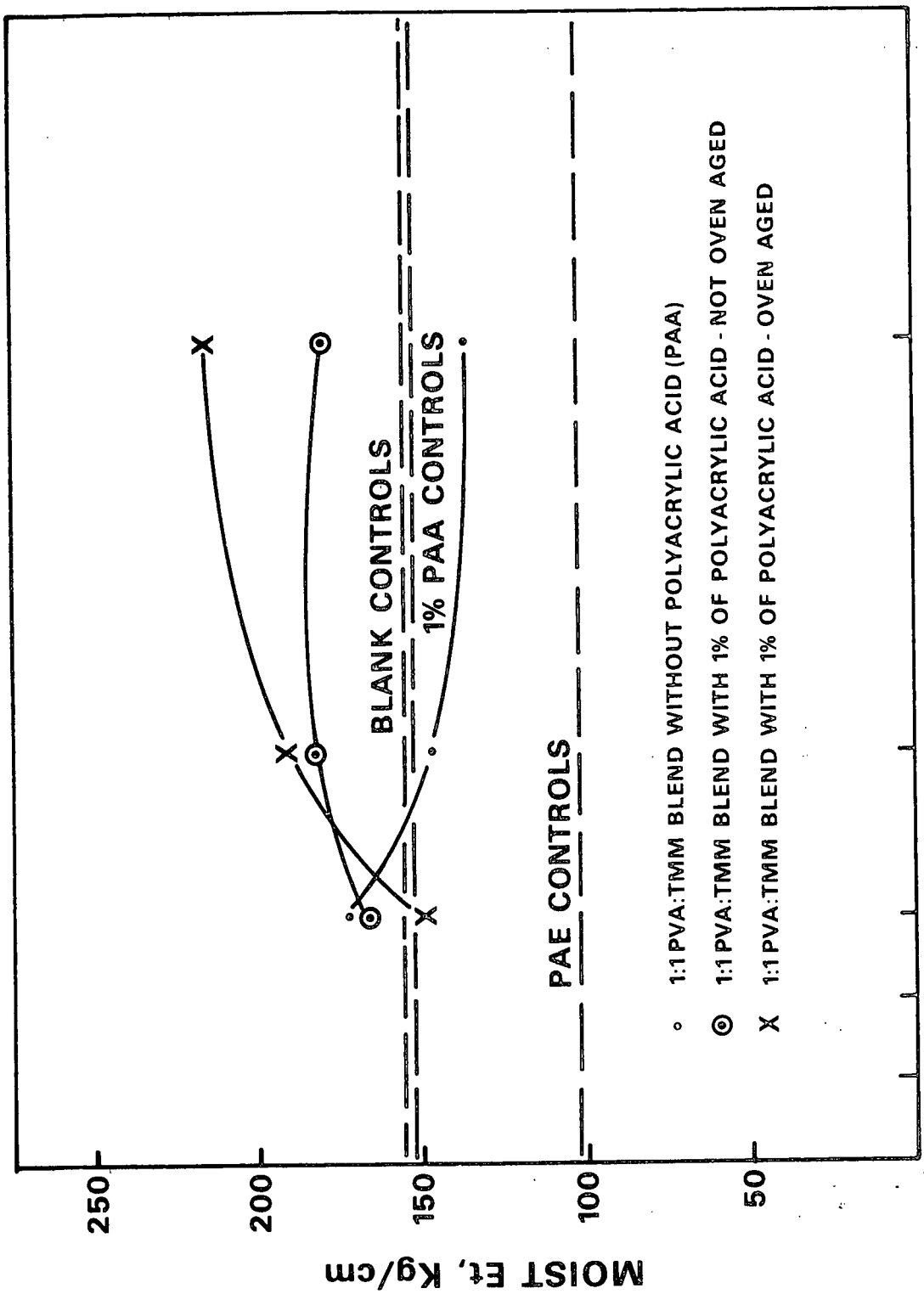


Figure 42. The effect of PVA:PAE addition level on moist extensional stiffness (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

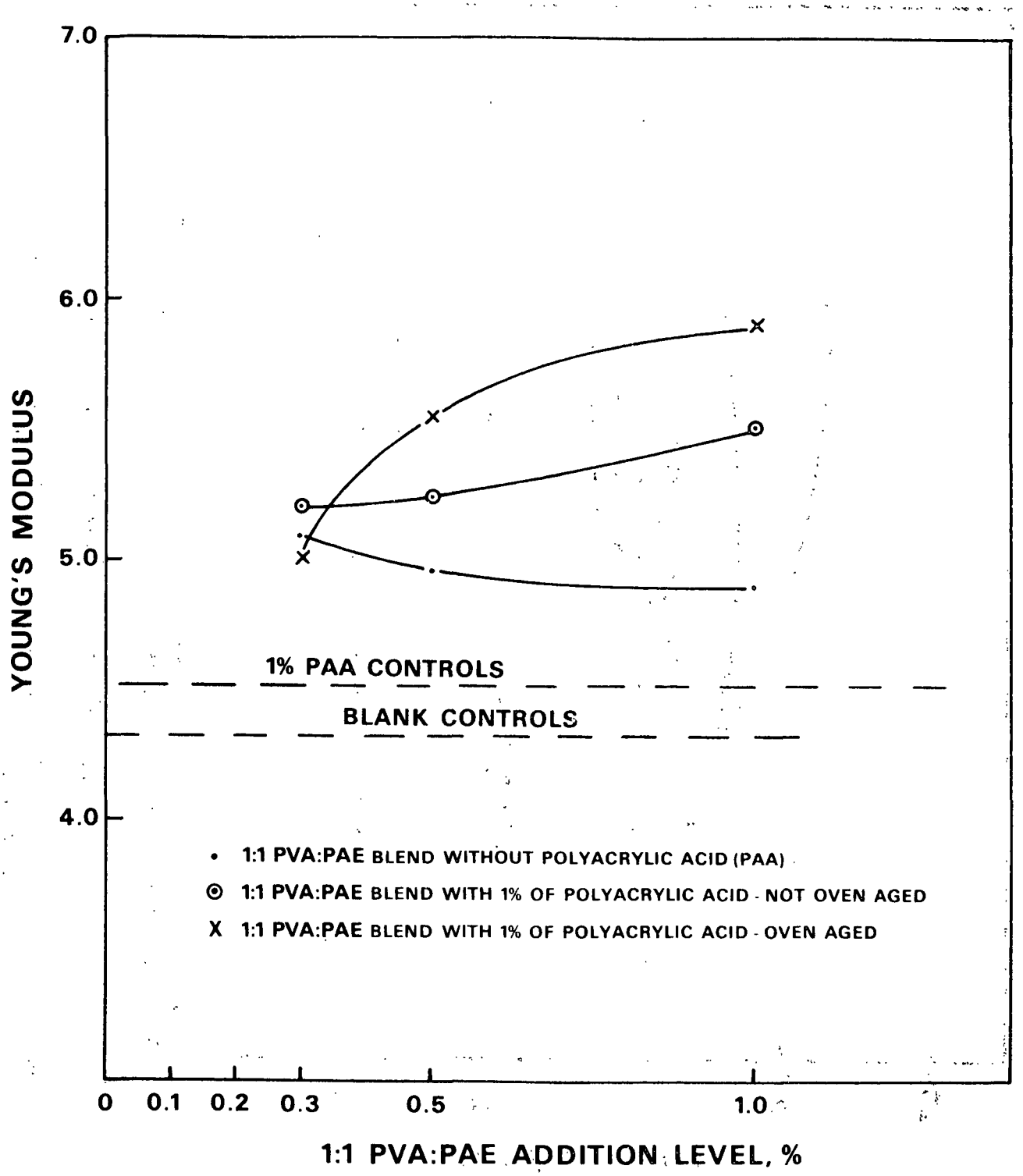


Figure 43. The effect of PVA:PAE addition level on Young's modulus (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

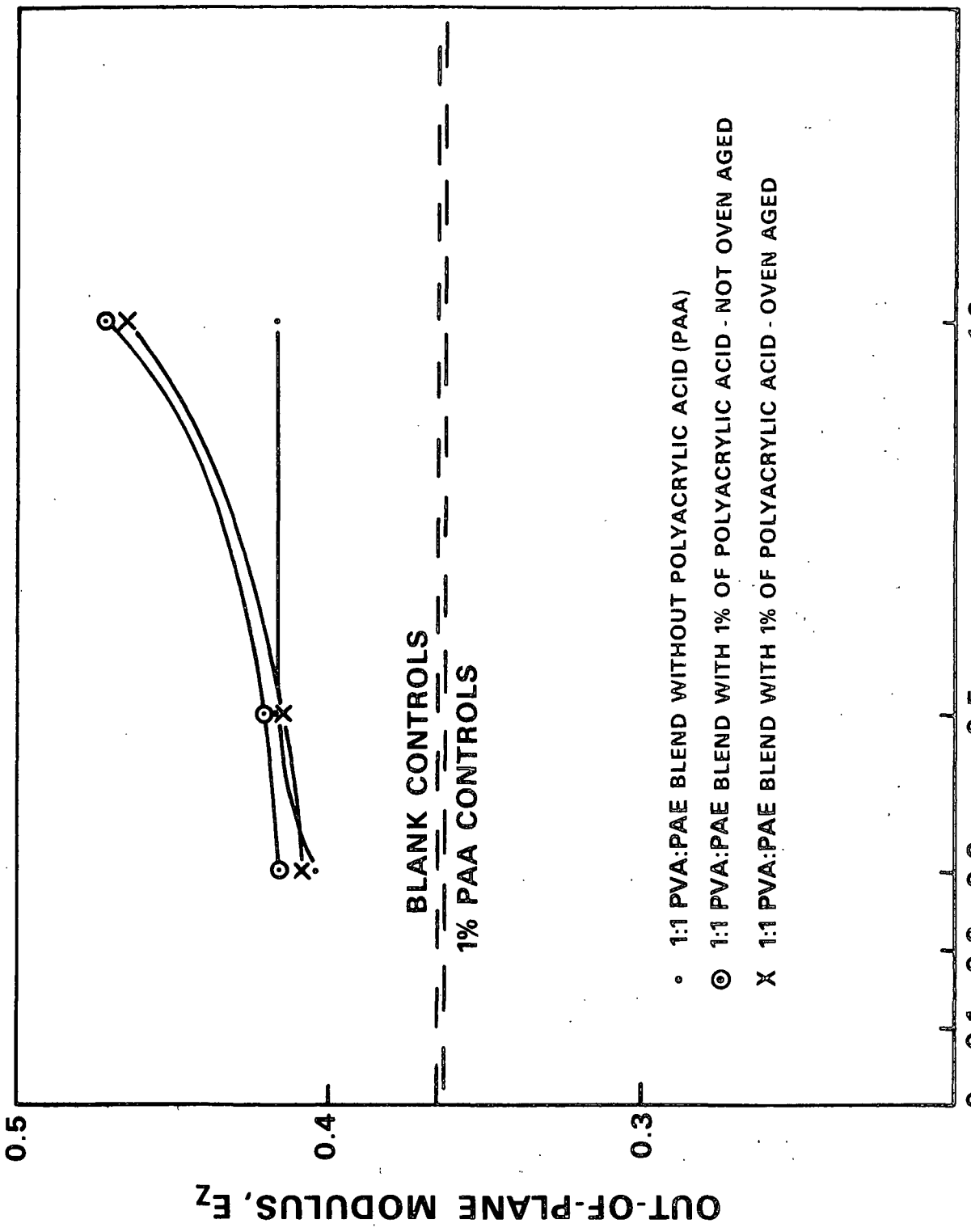


Figure 44. The effect of PVA:PAE addition level on out-of-plane modulus (classified unbleached kraft - 48.8% yield; kappa No. 33.7).

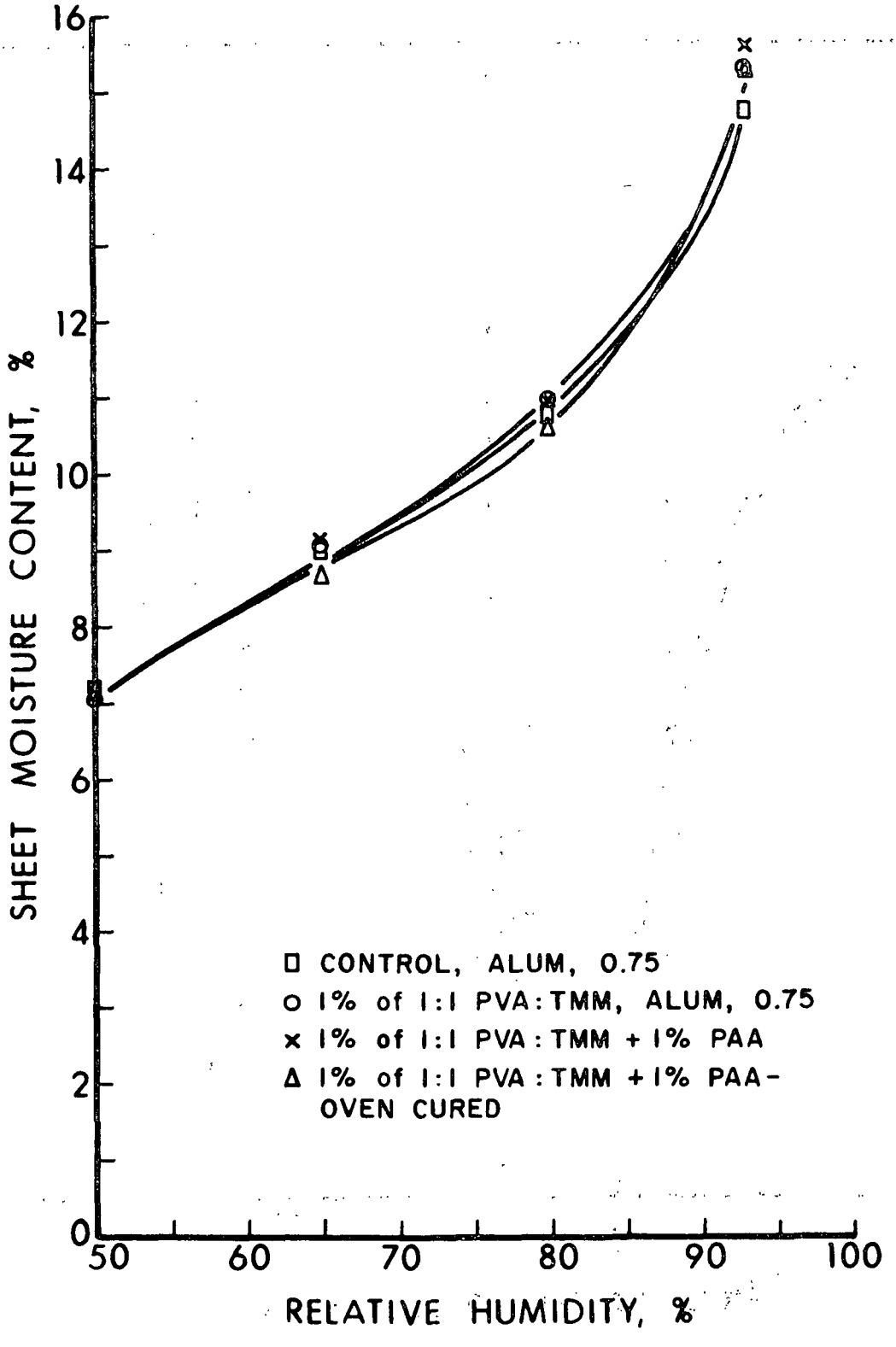


Figure 45. The effect of relative humidity on sheet moisture content (classified unbleached kraft - 48.8% yield; kappa No. 33.7; PVA/TMM combinations).

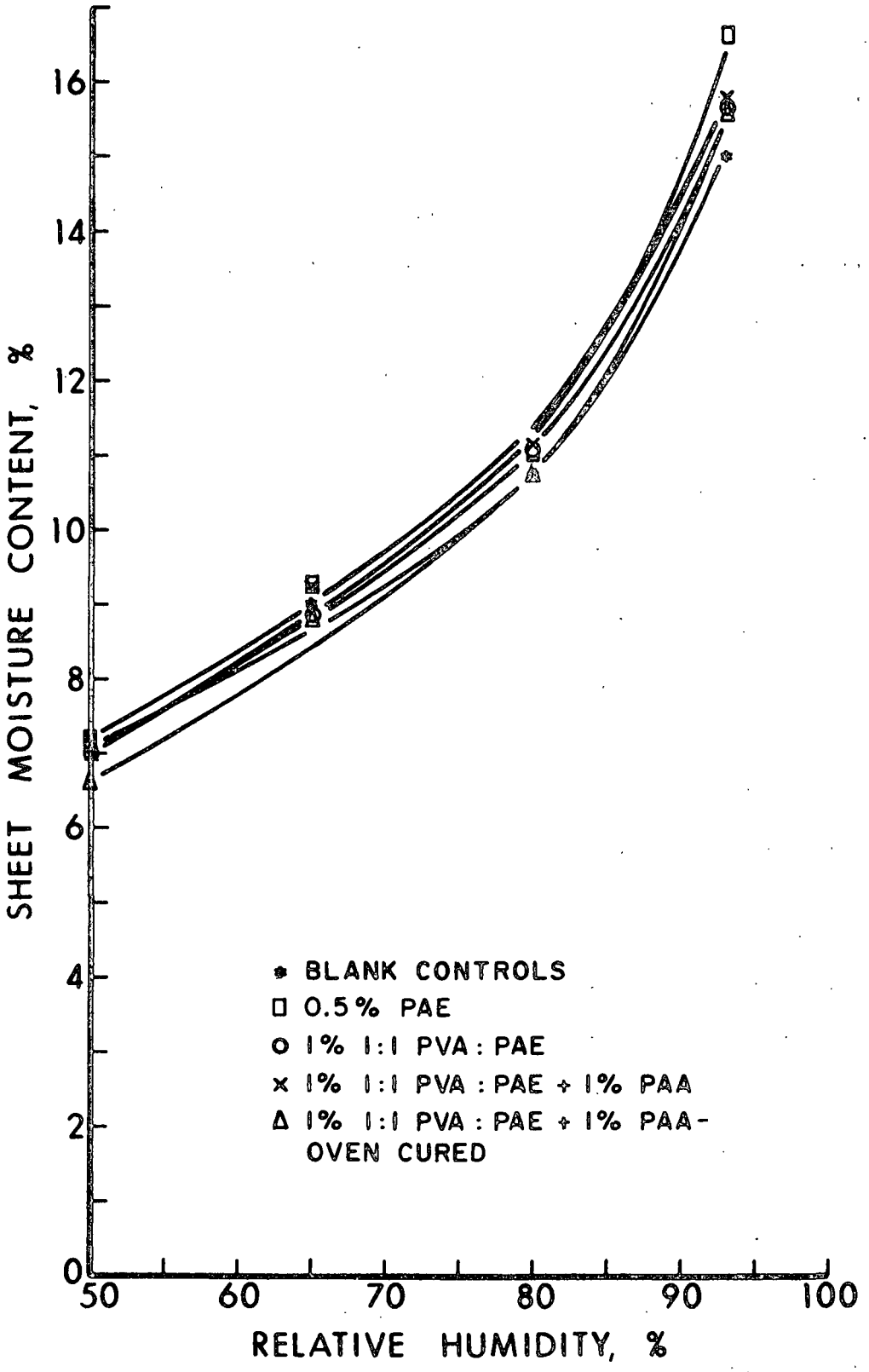


Figure 46. The effect of relative humidity on sheet moisture content (classifed unbleached kraft - 48.8% yield; kappa No. 33.7; PVA/PAE combinations).

not necessarily represent stoichiometric proportions. Further, substantial reductions in additive costs could be realized at lower PAA levels. Therefore, primarily on the basis of cost, the decision was made to substitute guar gum and unmodified cornstarch as the third polymer, considering that the third material may be retained through a coflocculation mechanism involving PAE and PAA. Guar gum and starch are known to be effective fiber bonding agents. Results are recorded in Table 10. Note: The pulp from cook No. 2 had aged several months since first used in handsheet preparations. Accordingly, the decision was made to prepare fresh blank controls and 1% PAE reference controls. Physical test results for these sets are included in Table 10.

The results in Table 10 indicate that the primary components are PAE and PAA (Set 61) and the third polymer provides, at best, a modest advantage in some tensile properties, i.e., moist and wet tensile. In fact, the lowest cost component (starch) proved marginally better than guar gum, whereas polyvinyl alcohol provided no advantage at all.

The final unit of work with the PAE/PAA system examined the effect of PAA addition level or PAA/PAE ratio and molecular weight on strength properties. A brief examination of the effect of fines was included. Results are presented in Table 11. Strength properties as a function of PAA addition level and molecular weight are plotted in Fig. 47-56.

CHEMICAL ANALYSIS

Numerous efforts were made to determine the mechanism by which the two major polymer systems (PAE/CMC and PAE/PAA) produced high levels of strength properties in paper. More specifically, the goal of this part of the program was to establish, if possible, if ionic or covalent bonding was involved in the strength enhancement.

Table 10. A comparison of polymer combinations containing polyacrylic acid-classified softwood unbleached kraft pulp (pulp - cook No. 2, 47.2% yield, kappa No. 34.3).

Set No.	Additives, % based on fiber	Basis Wt., g/m²	Thickness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD	Moist Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD
59	Blank controls	63.6	163	0.390	2.88	0.171	2.30	0.288	242	26.5	1.81	0.123	1.45	0.143	1.80	0.130	107	15.5	2.69	0.180
60	PAE, 1.0	62.7	167	0.386	4.50	0.389	4.91	0.389	273	12.3	2.57	0.240	2.52	0.187	4.84	0.371	124	4.95	3.42	0.146
61	PAE, 0.5; PAA, 0.1	61.9	149	0.416	5.90	0.278	7.78	0.320	326	30.2	3.16	0.092	3.73	0.285	5.67	0.675	148	15.5	4.09	0.218
62	1:1 PVA:PAE, 1.0; PAA, 0.1	60.2	154	0.388	5.30	0.246	6.14	0.756	286	23.9	2.94	0.181	3.39	0.169	4.76	0.429	130	11.9	4.10	0.189
63	1:1 Guar gum:PAE, 1.0; PAA, 0.1	67.0	163	0.412	5.85	0.282	7.86	0.772	366	13.9	2.99	0.171	3.84	0.106	6.54	0.186	161	3.49	4.14	0.089
64	1:1 Starch[a]:PAE, 1.0;PAA,0.1	64.2	156	0.412	5.76	0.474	7.94	0.778	324	23.5	3.14	0.182	3.97	0.245	6.61	0.451	167	9.30	4.20	0.178

Set No.	Additives, % based on fiber	Moist Tensile Factor	Wet Breaking Length km	SD	Wet Tensile Factor
59	Blank controls	1.0	0.062	0.006	1.0
60	PAE, 1.0	1.74	0.92	0.057	14.84
61	PAE, 0.5; PAA, 0.1	2.57	1.12	0.255	18.06
62	1:1 PVA:PAE, 1.0; PAA, 0.1	2.33	1.19	0.043	19.19
63	1:1 Guar gum:PAE, 1.0; PAA, 0.1	2.65	1.34	0.055	21.61
64	1:1 Starch[a]:PAE, 1.0;PAA,0.1	2.74	1.39	0.061	22.42

[a]Unmodified cornstarch.

Table 11. The effect of PAA/PAE ratio and PAA molecular weight on paper strength properties - softwood unbleached kraft pulp (pulp - cook No. 2, 47.2% yield; kappa No. 34.3).

Set No.	Additive, % based on fiber	PAA/PAE Ratio	Basis Wt., g/m²	Thick-ness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length km	SD	TEA kg m/m2	SD	Et kg/cm	SD	Stretch %	SD
59	Blank controls (classified pulp)	--	63.6	163	0.390	2.88	0.171	2.30	0.288	242	26.5	1.81	0.123
60	PAE, 1.0	--	62.7	167	0.386	4.50	0.389	4.91	0.389	273	12.3	2.57	0.240
65	PAE, 0.5; PAA[a], 0.05	0.1	64.2	158	0.405	4.96	0.416	6.43	1.13	307	31.1	2.91	0.327
66	PAE, 0.5; PAA[a], 0.10	0.2	63.7	157	0.406	5.32	0.322	7.37	0.996	301	18.7	3.13	0.263
67	PAE, 0.5; PAA[a], 0.2	0.4	63.4	153	0.413	5.66	0.320	7.79	0.702	320	18.2	3.24	0.134
68	PAE, 0.5; PAA[a], 0.5	1.0	61.8	149	0.414	5.51	0.532	6.60	0.918	337	21.1	2.84	0.227
69	PAE, 0.5; PAA[b], 0.1	0.2	60.1	155	0.388	4.57	0.358	5.76	0.887	246	8.22	3.06	0.272
70	PAE, 0.5; PAA[c], 0.1	0.2	68.9	162	0.426	5.35	0.254	7.94	0.498	332	12.2	3.19	0.090
71	PAE, 0.5; PAA[a], 0.1 (whole pulp)	0.2	62.4	140	0.446	6.19	0.450	8.98	1.01	335	21.9	3.39	0.210

[a]Molecular weight of PAA 104,000.
[b]Molecular weight of PAA 5,100.
[c]Molecular weight of PAA 300,000-500,000.

Set No.	Additive, % based on fiber	Moist Strength Properties: Breaking Length km	SD	TEA kg m/m²	SD	Et kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Wet Breaking Length km	SD	Wet Tensile Factor
59	Blank controls (classified pulp)	1.45	0.143	1.80	0.130	107	15.5	2.69	0.180	1.0	0.062	0.006	1.0
60	PAE, 1.0	2.52	0.187	4.84	0.371	124	4.95	3.42	0.146	1.74	0.92	0.057	14.84
65	PAE, 0.5; PAA[a], 0.05	3.37	0.281	5.89	0.720	144	16.9	4.39	0.176	2.32	1.23	0.087	19.84
66	PAE, 0.5; PAA[a], 0.10	3.06	0.190	5.34	0.616	130	14.8	4.37	0.275	2.11	1.13	0.025	18.23
67	PAE, 0.5; PAA[a], 0.2	3.07	0.306	5.24	0.835	140	19.7	4.14	0.482	2.12	1.09	0.054	17.58
68	PAE, 0.5; PAA[a], 0.5	3.17	0.201	5.09	0.571	130	11.0	4.01	0.253	2.19	1.09	0.087	17.58
69	PAE, 0.5; PAA[b], 0.1	2.83	0.288	4.36	0.613	104	4.52	4.10	0.326	1.95	1.10	0.063	17.74
70	PAE, 0.5; PAA[c], 0.1	3.14	0.196	5.71	0.505	127	22.2	4.51	0.147	2.17	1.08	0.060	17.42
71	PAE, 0.5; PAA[a], 0.1 (whole pulp)	4.12[d]	0.297	7.50	0.690	161	24.9	5.00	0.103	1.79	1.23[e]	0.033	10.70

[a]Molecular weight of PAA 104,000.
[b]Molecular weight of PAA 5,100.
[c]Molecular weight of PAA 300,000-500,000.
[d]Moist control was 2.30 km.
[e]Wet control was 0.115 km.

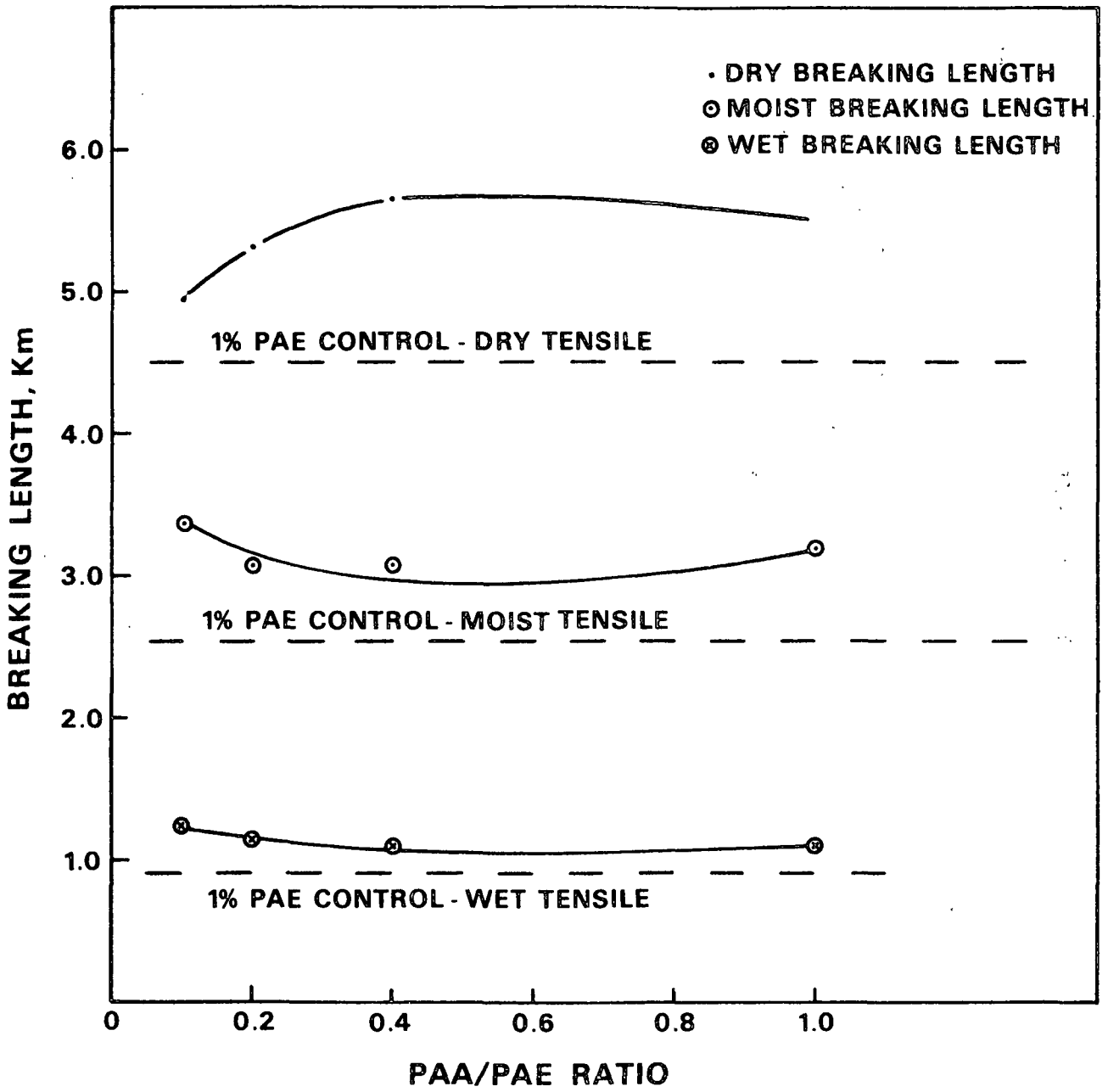


Figure 47. The effect of PAA/PAE ratio on breaking length at a constant PAE addition of 0.5% (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

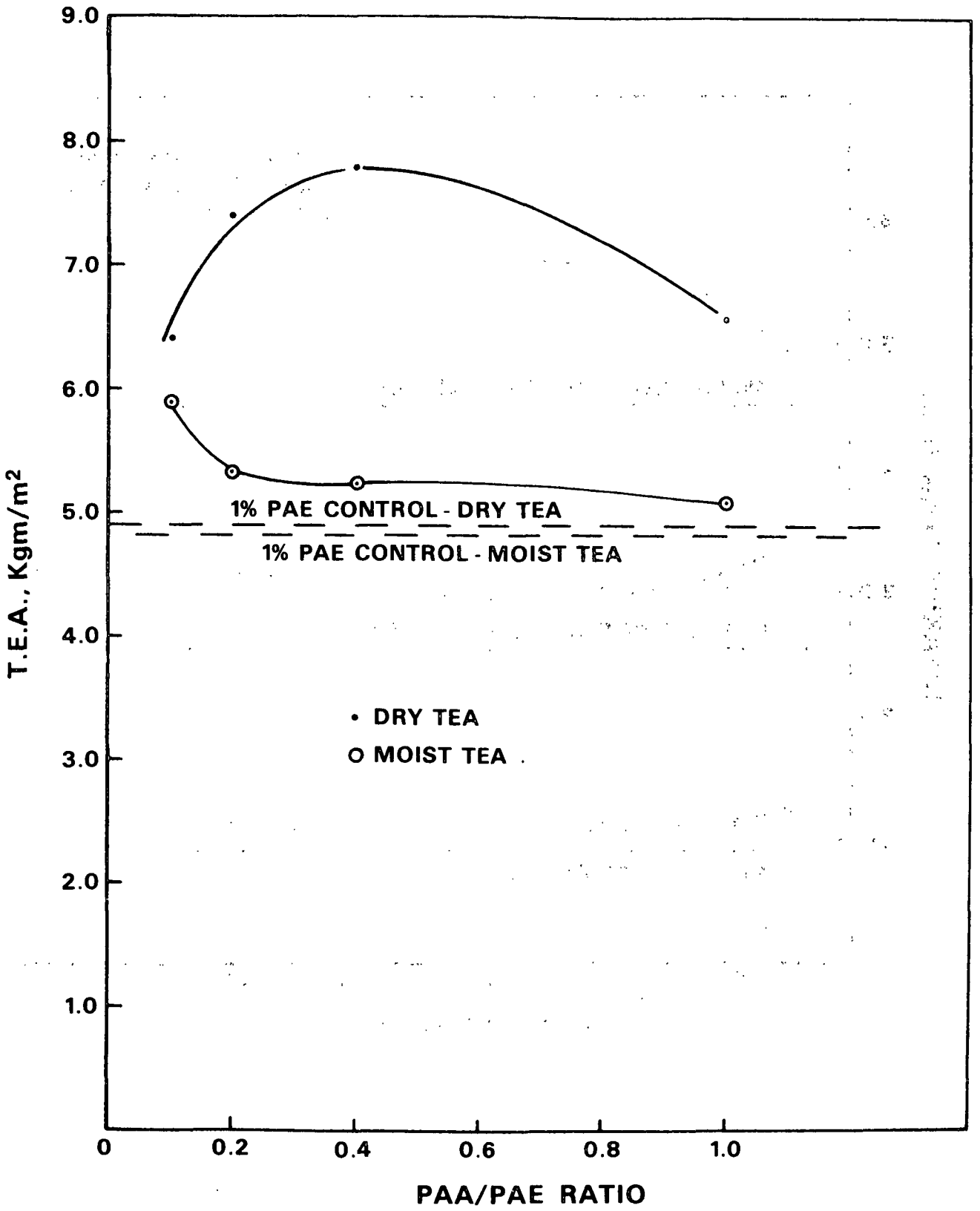


Figure 48. The effect of PAA/PAE ratio on TEA at a constant PAE addition of 0.5% (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

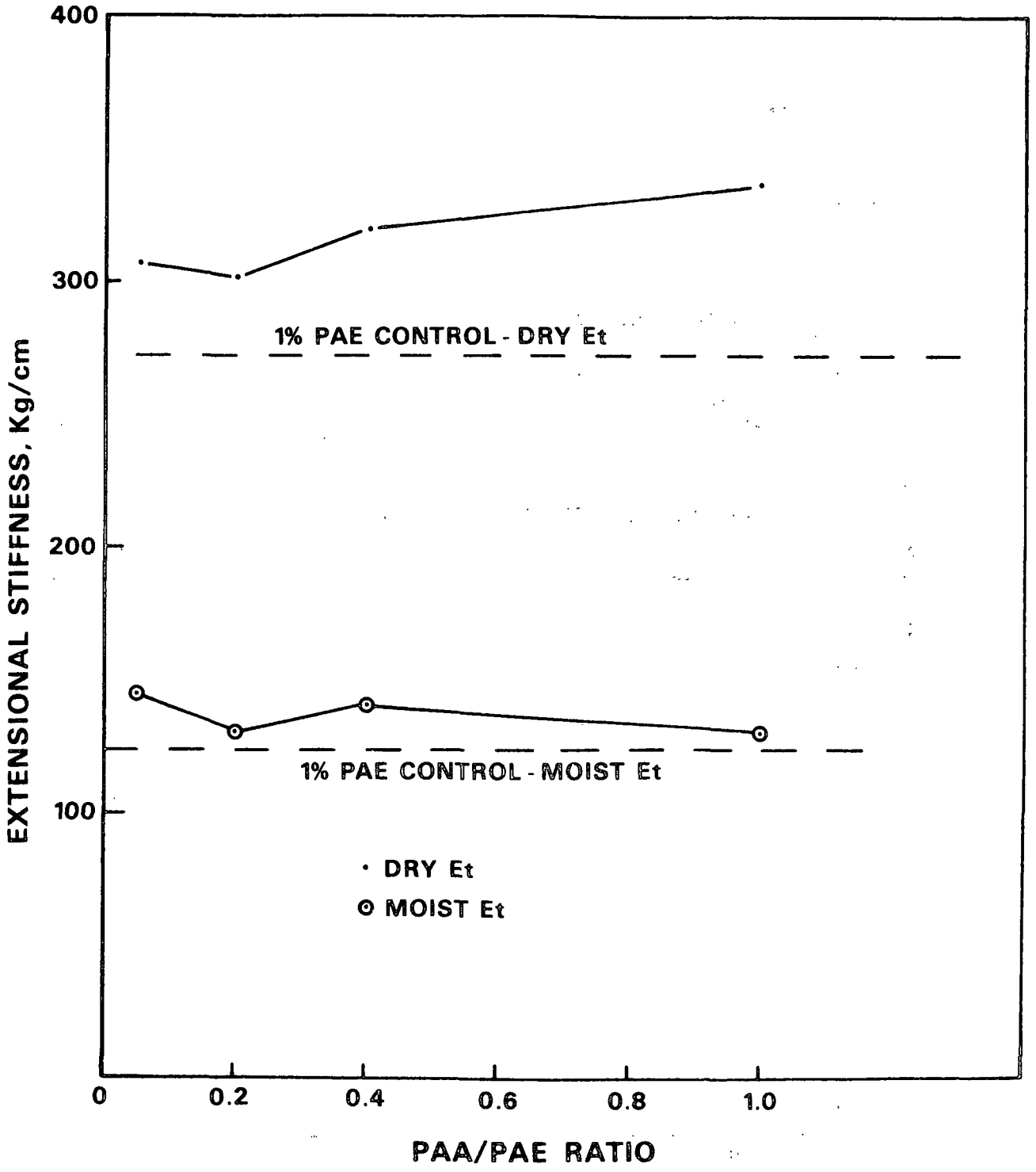


Figure 49. The effect of PAA/PAE ratio on extensional stiffness at a constant PAE addition of 0.5% (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

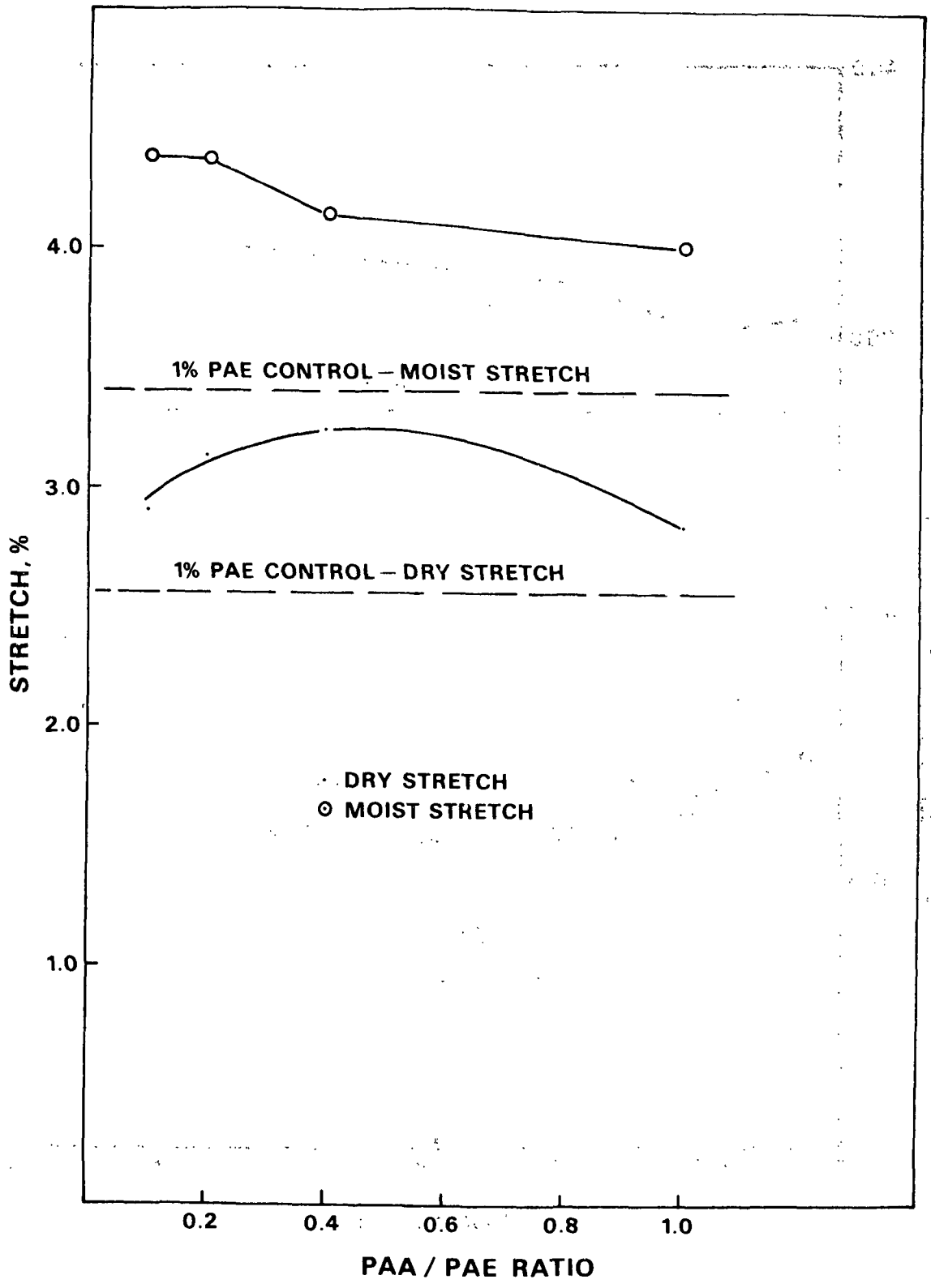


Figure 50. The effect of PAA/PAE ratio on stretch at a constant PAE addition of 0.5% (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

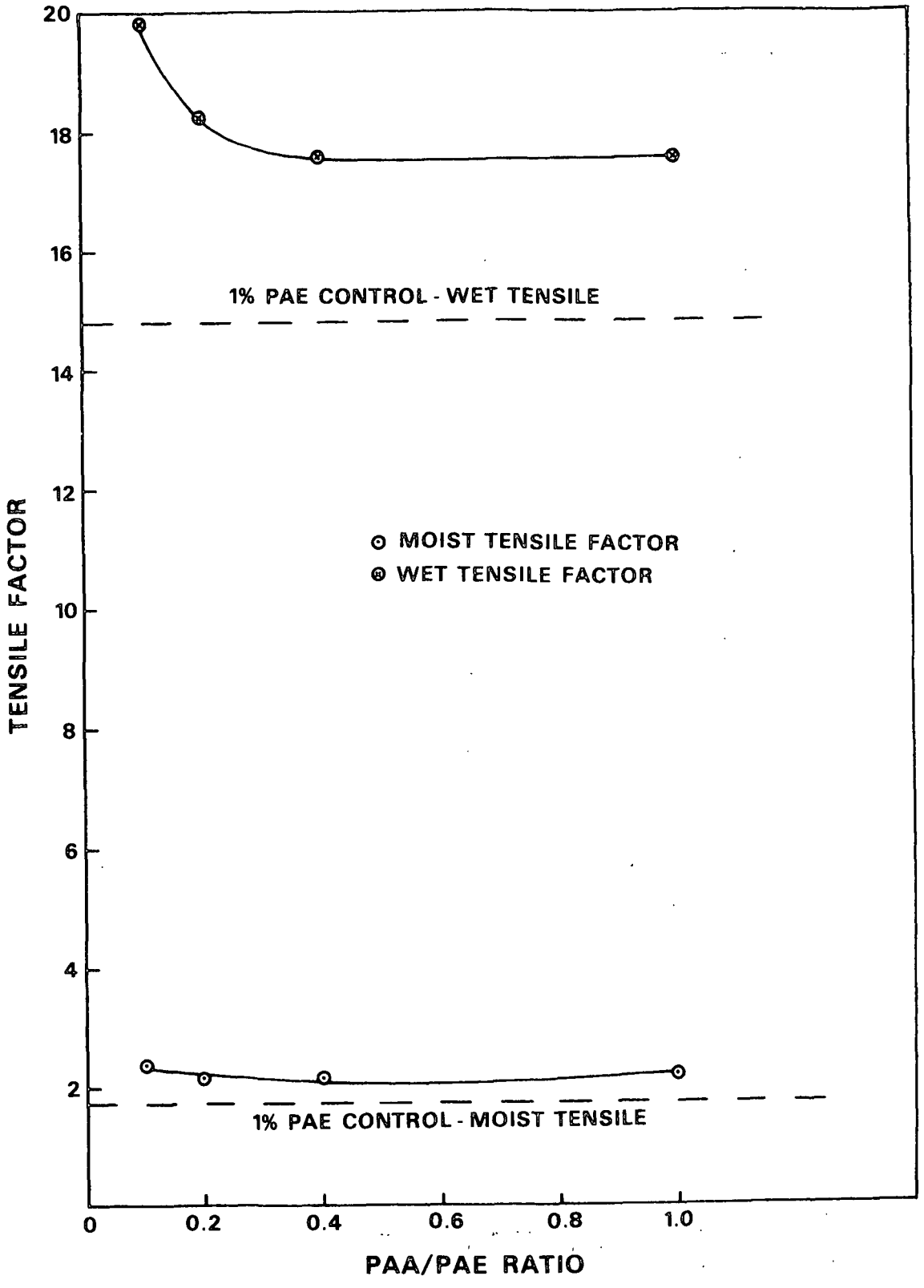


Figure 51. The effect of PAA/PAE ratio on tensile factors at a constant PAE addition of 0.5% (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

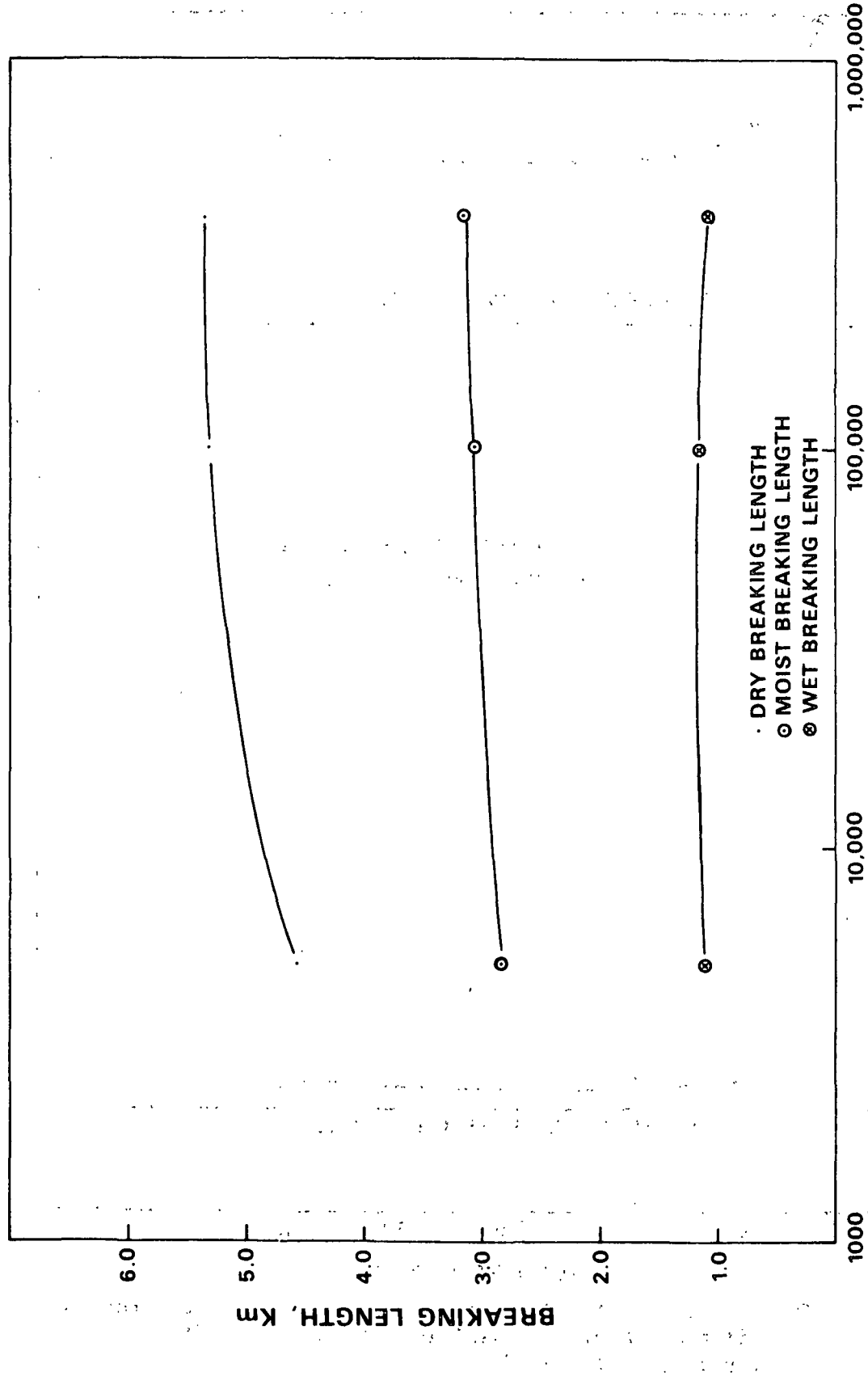


Figure 52. The effect of PAA molecular weight on tensile strength: % addition level, PAE, 0.5; PAA, 0.1 (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

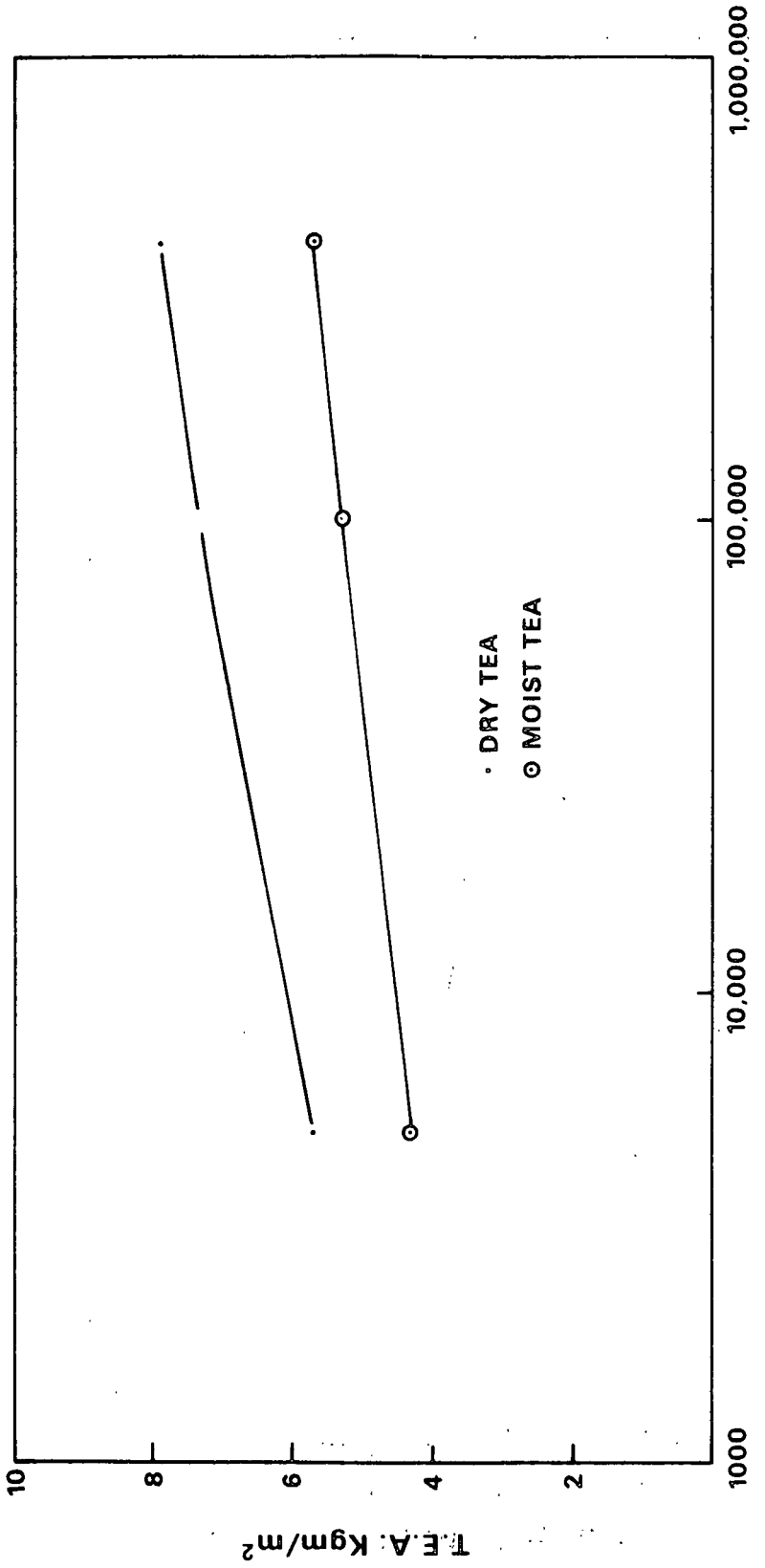


Figure 53. The effect of PAA molecular weight on tensile energy absorption: % addition level, PAE, 0.5; PAA, 0.1 (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

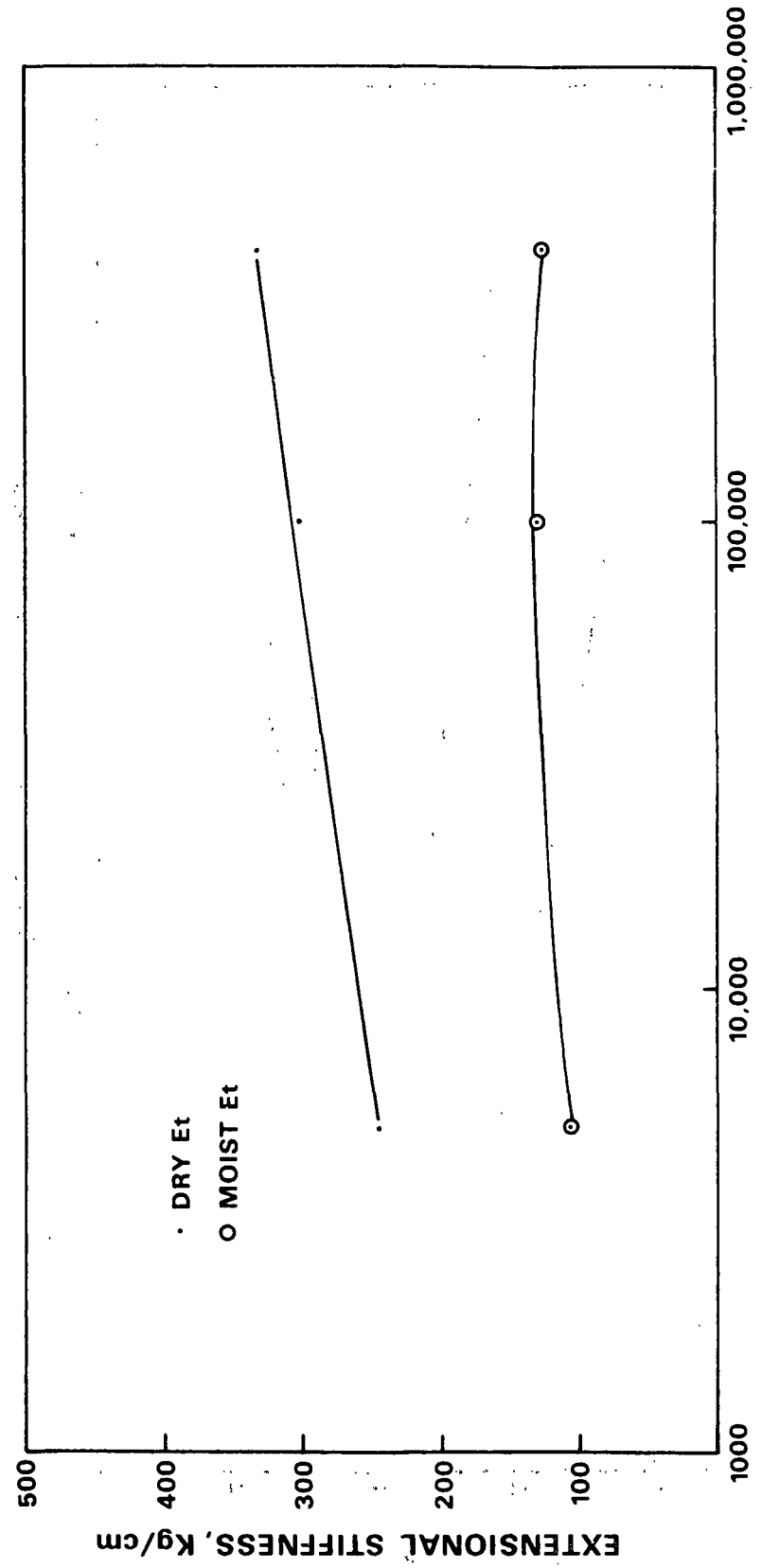


Figure 54. The effect of PAA molecular weight on extensional stiffness: % addition level; PAE, 0.5; PAA, 0.1 (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

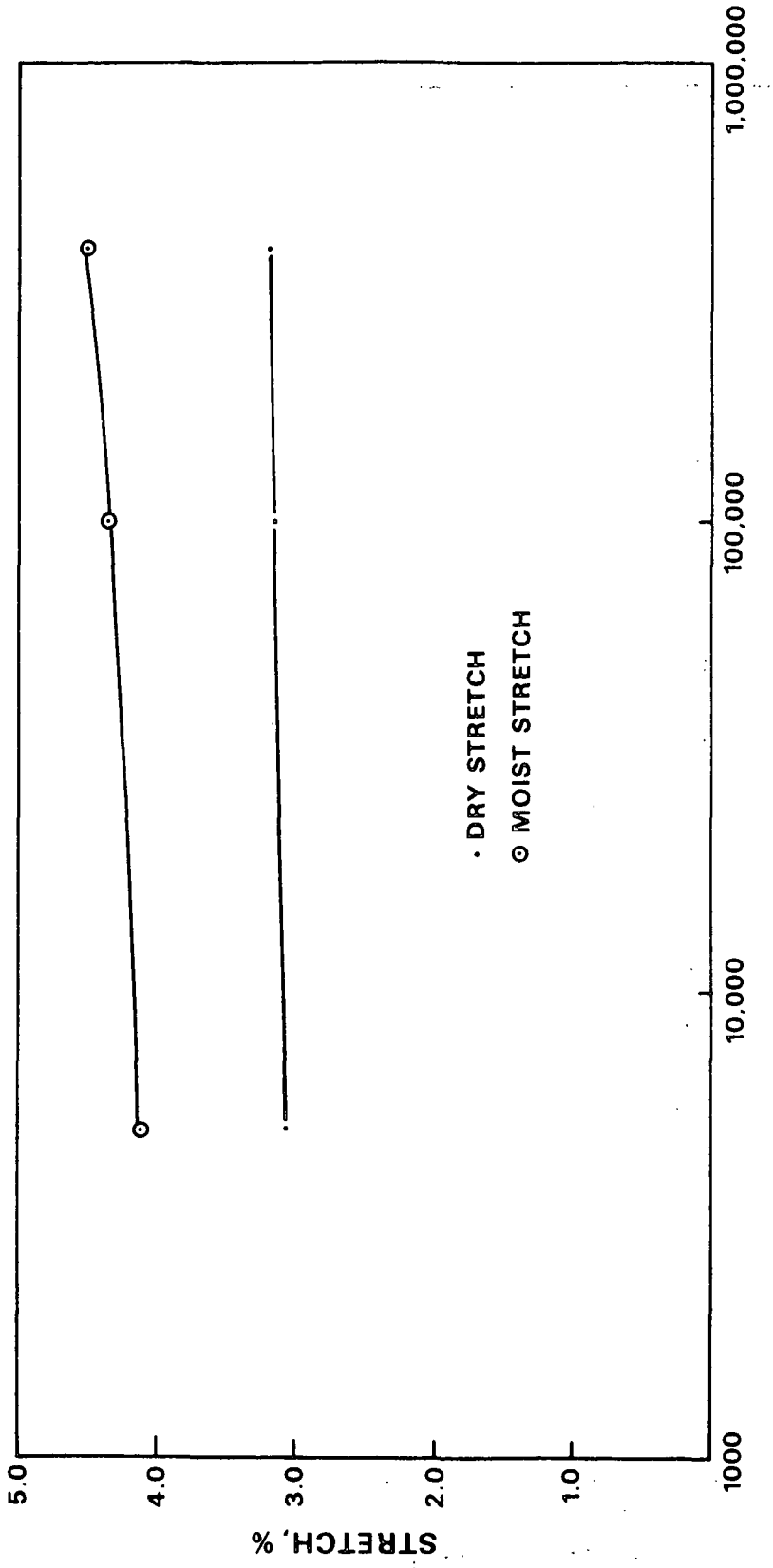


Figure 55. The effect of PAA molecular weight on stretch: % addition level; PAE, 0.5; PAA, 0.1 (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

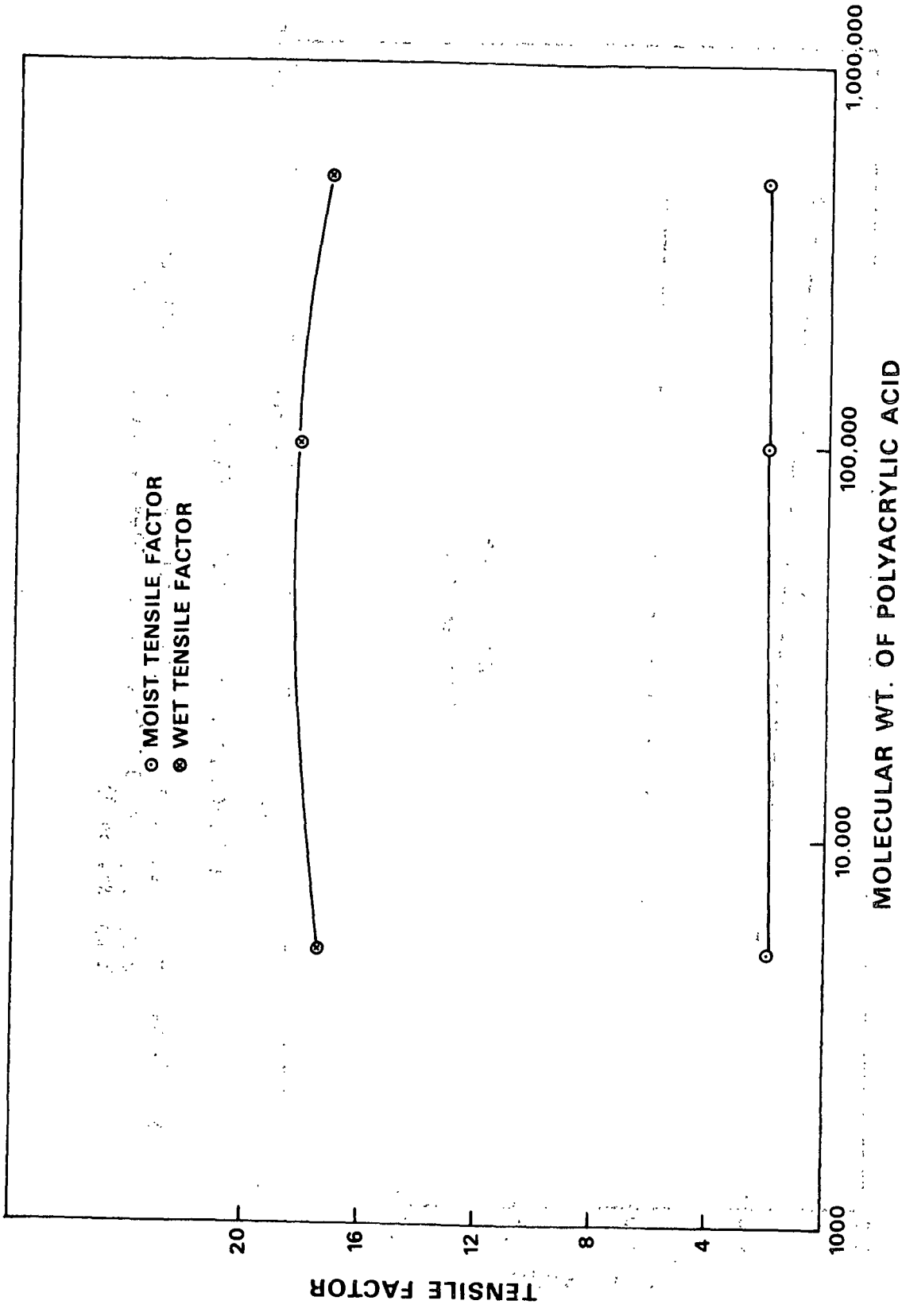


Figure 56. The effect of PAA molecular weight on moist and wet tensile factors, addition level; PAE, 0.5; PAA, 0.1 (classified unbleached kraft - 47.2% yield; kappa No. 34.3).

Samples of treated papers and reference chemical controls were submitted to a private laboratory for ESCA (Electron Spectroscopy for Chemical Analysis), since this equipment was not available at the Institute. The materials submitted for analysis included unbleached kraft handsheets and plasticizer-free cellophane, which were treated with PAE and combinations of PAE and CMC or PAA. The cellophane samples were prepared by immersing in 3% solutions of the components with washing between each application where multicomponent systems were involved. After the final washing, the treated cellophane was air dried and then oven aged 10 min. at 105°C. Handsheets from unbleached southern pine kraft pulp were prepared incorporating the following components:

1. 1.0% of PAE,
2. 1.0% of PAE + 0.4% of CMC, and
3. 0.5% of PAE + 0.1% of PAA

ESCA provided an elemental analysis of the top 100Å of sample surface and the results are recorded in Table 12. Table 12 includes the PAE content at the surface based on the ESCA data and the PAE content in the whole sample based on weight as determined by GLC/mass spectroscopy. Thus, these analyses provided information relative to PAE content at the surface and within the whole sample, but information concerned with bonding mechanisms could not be derived from these data.

Fourier Transform Infrared (FTIR) analysis was used extensively in an effort to provide the desired information. Both transmission and surface reflectance approaches including multiple internal reflectance (MIR) were employed in FTIR analyses. In conducting these tests, PAE, PAE/CMC, and PAE/PAA were used in both the solid or powdered forms and as films cast on a variety of substrates including glass, Teflon, steel, cellophane, and paper. The purpose

Table 12. Elemental analysis of treated cellophane and handsheets by ESCA.

Sample	Identification	Element, atom % units							PAE Content at Surface, %	PAE Content in Whole Sample Based on Weight, GLC/mass spec. %
		Carbon	Oxygen	Nitrogen	Chlorine	Sodium	Sulfur	Fluorine		
1	Cellophane control	66.0	34.0	--	--	--	--	--	--	--
2	Cellophane - 3% PAE	65.0	34.0	1.4	0.1	--	--	--	11.6	--
3	Cellophane - 3% PAE + 3% CMC	68.0	30.0	1.7	0.2	--	--	--	14.1	--
4	Cellophane - 3% PAE + 3% PAA	66.0	29.0	4.7	0.3	--	--	--	38.9	--
7	Handhseet control	63.0	37.0	--	--	--	--	--	--	--
5	Handsheet - 1% PAE	65.0	34.0	1.4	--	--	---	--	11.6	0.81
6	Handsheet - 0.5% PAE, 0.1% PAA	63.0	34.0	1.4	0.3	--	--	0.6	11.6	0.61
8	Handsheet - 1.0% PAE, 0.4% CMC	66.0	31.0	2.1	--	--	--	--	17.5	0.91
9	PAE control	68.0	15.0	12.0	4.3	--	Trace	--	--	--
10	PAA control	63.0	36.0	--	--	0.8	0.2	--	--	--
11	CMC control	64.0	30.0	--	--	6.1	--	--	--	--

in using steel and other noncellulosic substrates was to eliminate the possibility of bonding to cellulose but provide the opportunity for interaction among the polymeric components themselves. Efforts to use transmission FTIR failed due to the masking effect of cellulose, when present. The prevailing problem in most attempts to use surface reflectance and MIR was the inability to duplicate results. Finally, samples of Whatman filter paper and glass fiber filters were immersed for 2, 5, and 10 seconds in a 1% solution of PAE, 1% PAE followed by 0.4% CMC, and 1% PAE followed by 0.2% PAA. The treated samples were first air dried and then oven dried as previously described. Analysis was then made by diffuse reflectance FTIR, and the ratio of the 1740 ester band/1650 amide band was measured. This provides a measure of ester formation and hence, covalent bonding. The results of the analysis for each time interval are presented in Table 13. Since a consistent trend with respect to time of treatment was not evident in Table 13, the decision was made to average the results for all time periods, and this summation is recorded in Table 14.

REPULPABILITY STUDIES

The relative repulpability of unbleached softwood kraft handsheets containing PAE, PAE/CMC, and PAE/PAA was examined for repulpability employing an arbitrary procedure based on literature provided by the supplier of the PAE resin. The procedure consisted of the following steps:

1. Five gram samples of handsheets cut into 0.5 in. squares were added to a beaker containing 500 mL of tap water adjusted to pH 11 with NaOH or to pH 7 in the presence of 2% of sodium hypochlorite based on fiber weight.
2. The paper samples were heated over steam for 30 min with moderate agitation provided by a Lightning stirrer. Samples

at pH 11 were heated to 150°F, samples at pH 7 were heated to 120°F. The pH and temperature were maintained at the indicated levels throughout the treatment period.

3. The material was transferred to a Waring Blendor and treated for one minute at high speed. Two hundred and fifty mL of treated stock was then removed to form a 2.5-g Noble and Wood handsheet (63 g/m^2).
4. Two hundred and fifty mL of pH adjusted water was added to the blender followed by an additional treatment of two minutes at high speed for a total treatment of three minutes.
5. The pulp in the blender was then used to form a second 2.5-g handsheet.

Table 13. Diffuse reflectance FTIR analysis of treated substrates.

Additive, % solids	Substrate	Contact Time, s	A_{1740}(Ester)/A_{1650}(Amide I) Ratio		
			Set A	Set B	Average
1% PAE	Paper[a]	2	--	0.043	--
		5	--	0.036	--
		10	0.056	0.058	0.057
	Glass fiber[b]	2	0.080	0.072	0.076
		5	0.069	0.072	0.070
		10	0.067	0.072	0.070
1% PAE followed by 0.4% CMC	Paper[a]	2	0.176	0.187	0.181
		5	0.171	0.169	0.170
		10	0.204	0.240	0.222
	Glass fiber[b]	2	0.114	0.136	0.125
		5	0.199	0.130	0.164
		10	0.204	0.145	0.174
1% PAE followed by 0.2% PAA	Paper[a]	2	0.106	0.146	0.126
		5	0.163	0.204	0.184
		10	0.186	0.106	0.146
	Glass fiber[b]	2	0.088	0.098	0.093
		5	0.100	0.118	0.109
		10	0.093	0.113	0.103

[a]Whatman No. 1 filter paper.
[b]Glass filter paper.

The handsheets were pressed and dried in the prescribed manner and those from the 3-min blender treatment were tested for uniformity by the Thwing formation test. Results are presented in Table 15. (Note: handsheets prepared from the 1-minute treatment interval were very irregular and were not tested.)

Table 14. Summary of diffuse reflectance FTIR analysis.

Additive, % solids	Substrate	A_{1740}/A_{1650}
1% PAE (control)	Paper	0.048 ± 0.010
	Glass fiber	0.072 ± 0.004
1% PAE + 0.4% CMC	Paper	0.191 ± 0.027
	Glass fiber	0.155 ± 0.034
1% PAE + 0.2% PAA	Paper	0.152 ± 0.033
	Glass fiber	0.106 ± 0.008

NOTES: The A_{1740}/A_{1650} ratios listed above represent the average of 4 or 6 determinations. The differences listed for the PAE controls are probably not meaningful since the method was at or near the limits of resolution.

Table 15. Repulpability of handsheets treated with combinations containing PAE (unbl. softwood kraft pulp).

Description, additives, % based on fiber	Thwing Formation Number	
	Repulped at pH 11 and 66°C	Repulped at pH 7 and 50° C with 2% sodium hypochlorite
Control (oven aged)	--	32.9[a]
PAE, 1.0	29.8	27.5
CMC/PAE (Ratio 0.4), 1.4	28.4	20.4
1:1 PVA:PAE, 1.0; PAA, 1.0 (oven aged)	27.3	24.8

[a]Repulped at pH 7 without hypochlorite.

DISCUSSION OF RESULTS

Results in Table 1 and Fig. 1-3 show that significant increases in tensile properties can be achieved in a high alpha pulp with CMC/PAE combinations depending upon the amount and ratio employed. In general, high addition levels are required to produce substantial strength improvements in this type of pulp as is evident from the current results. Moist and wet tensile factors reached values of 2.66 and 17.5, respectively, compared to values of 1 and 2-3 for the PAE controls. An optimum CMC/PAE ratio of 0.4 was reported by Espy (22), and, while this applies at the 2.5% PAE addition level, it does not necessarily apply at other additions. This is particularly evident in wet tensile strength at the 1% PAE addition level, where the high tensile values were achieved at CMC/PAE ratios of 0.4 and 2.0. According to Espy (22), the optimum ratio appears to provide a neutral or slightly cationic precipitate which deposits in quantity on the fiber. With PAE resin alone, some of the strength increment may be due to its reaction with carboxyl groups in the pulp; some to self cross-linking. In the presence of CMC, the PAE resin can form ionic carboxyl complexes which can improve dry strength. Upon drying, these have been found to form some ester linkages which, being covalent, can impart wet strength as well as dry strength.

When utilizing CMC/PAE combinations in an average yield unbleached softwood kraft pulp at significantly reduced addition levels compared with the high-alpha pulp (Table 3, Fig. 4-9), it becomes evident that these additive combinations again produced substantial improvements over PAE not only in breaking length but also in other tensile properties including TEA and to some extent in Et, stretch, and in-plane moduli. For example, 1.4% of CMC/PAE improved dry

and moist TEA 50-60% over 1.5% PAE. Dry and moist Et and stretch were improved 15-20% under the same conditions. Similar increases (15-20%) were obtained in Young's and shear moduli. The percentage improvements for a given test were roughly comparable for the dry and moist conditions. This translates to paper with improved toughness, extensibility, and stiffness, all of which become important attributes to paper and/or board used under high humidity conditions.

Addition of CMC/PAE tended to increase sheet density which usually results in higher strength properties. Hence correcting the tensile values to a constant density (that of the blank controls) was a reasonable procedure. The results in Table 4 and Fig. 10 and 11 show that correcting to a constant density tended to reduce moist and wet tensile factors, but the original conclusions remain the same; i.e., selected treatments as in Sets 18, 19 and 21 provided substantial improvements over the PAE controls.

The effect of sheet moisture content as produced by relative humidities ranging from 50 to 93% is shown in Fig. 12. The purpose of this unit was to determine whether the treated papers adsorbed less moisture and were thereby capable of providing higher moist tensile factors. It is apparent from Fig. 6 that the CMC/PAE-treated papers had essentially the same moisture contents as those of the blank controls.

The effect of CMC/PAE ratio on paper properties at a constant total addition of 1% is shown in Table 5. In all tests, the CMC/PAE-treated papers were equal to, or superior to, the 1% PAE controls, depending upon the ratio. Several effects become evident in examining these results; (1) CMC/PAE ratio did not have a consistent effect on the properties examined, particularly moist tensile properties, and (2) the general level of strength achieved in this

series was somewhat lower than that obtained in the previous series. With respect to ratio, Espy (22) suggests that PAE predominates at CMC/PAE ratios up to approximately 0.4. At high CMC/PAE ratios, the combinations become anionic and are no longer adsorbed. The dependence of strength properties upon CMC/PAE ratio is related to the degree of substitution (DS) of the CMC, the charge density of the PAE resin and it is said to diminish in hard water as was used in the current program. With respect to the second effect, the reduced strength level is particularly evident in moist tensile properties. This may be due to differences in addition level and to the fact that the blank controls from the second batch of pulp (Cook No. 2) were weaker than those from Cook No. 1 in spite of the fact that yields, kappa numbers, and fiber lengths were quite similar. Reasons for the difference in response of the two pulps are not apparent. In general, the strength of the lab-prepared pulps was somewhat lower than that of commercial softwood unbleached kraft pulps.

Results to date with the CMC/PAE complex showed a lack of sizing (water resistance) among treated papers. This is not surprising, considering the polar nature and relatively high surface energy of the additives. Results in Table 6 show that the CMC/PAE-treated papers can be readily sized with dispersed rosin size in the presence of alum at pH 5.0-5.2 or with synthetic size at pH 8-9 with a relatively small decrease in tensile properties. Since the amount of sizing agent used in these tests produced hard sizing, it would be expected that the decline in strength could be minimized at lower sizing agent additions, particularly in the case of dispersed rosin size.

The final segment of work with CMC/PAE examined the effect of fines on the efficacy of the polymer combination. The results which are recorded in

Table 7 show that, as would be expected, handsheets formed from the whole pulp were stronger than those from the classified pulp. Since moist and wet tensile factors are determined by dividing the tensile results by those of the blank controls, the notably higher strength of the controls tended to diminish moist and wet tensile factors for the whole pulp compared to those of the classified pulp. In effect, the combination of additives was more effective relative to the controls in the classified pulp than in the whole pulp. Conceivably the strength additive was preferentially retained by the fines in the whole pulp and was not as available for interfiber bonding as in the classified pulp or, alternatively, variations in fines retention may have occurred with addition of CMC/PAE. These results suggest that CMC/PAE will be effective in lightly refined pulps which would benefit drainage and machine speed.

In pursuing the work of Zunker (23), 0.3, 0.5, and 1% of 1:1 combinations of PVA and TMM were examined in classified softwood unbleached kraft pulp. The results are presented in Table 8 and in Fig. 19-31. Papers containing PVA/TMM possessed superior strength properties compared to those containing PVA or TMM alone. Of course, PVA is not retained to an appreciable extent in the absence of a retention aid. In examining the data it will be seen that, in most cases, strength properties improved with PVA/TMM addition level in the absence of polyacrylic acid. The exceptions were dry and moist extensional stiffness, where little or no improvement was obtained. On the other hand, Young's modulus and out-of-plane modulus showed slight increases with addition level. It is also apparent in examining the data for this series that addition of 1% of polyacrylic acid under oven aged conditions further improved dry, moist, and wet breaking length but had little or no consistent effect on the remaining properties. According to Zunker (23), PVA provides the strength properties of a

long-chain polymer and TMM provides the cationic hook required for retention and/or reaction, although no chemical bonds are formed during the aqueous interaction of PVA and TMM. Instead, the PVA/TMM interaction products are intimate associations, entanglements, or complexes between the two components. Van der Waal's forces and/or hydrogen bonds are assumed to be involved. Thus by close proximity, the PVA polymer becomes associated with and benefits from the cationic charge on the oligomer molecules. The adsorption of PVA/TMM is relatively rapid and is assumed to be about 75-85% complete at typical papermaking consistencies.

A subsequent series of tests involved the use of 1:1 blends of PVA and PAE without and with polyacrylic acid. In this case PAE was used as the cationic component. The polyamide polyamine contains azetidinium groups which have the potential of forming esters with hydroxyl-bearing compounds such as cellulose and PVA. The inclusion of polyacrylic acid could enhance the potential of ester formation and covalent bonding. In this set of tests the same conditions were employed as in the previous series, i.e., 0.3, 0.5, and 1.0% additions of a 1:1 blend of PVA:PAE without and with the inclusion of 1% of polyacrylic acid. Results are presented in Table 9 and in Fig. 32-44.

In contrast to the PVA/TMM series, PVA/PAE provided little advantage over the PAE controls. This applies to all measured strength properties. However, in this case, the addition of 1% polyacrylic acid greatly increased strength properties including dry, moist, and wet tensile strength, TEA and, in most cases, stretch, extensional stiffness, and modulus (Young's and out-of-plane). In general, the oven aged papers provided higher strength properties although, in some cases, (dry TEA, stretch, Et, and out-of-plane modulus) the

nonaged papers containing PAA were roughly equivalent to the oven-aged papers. In general, higher strength and modulus levels were attained with PVA/PAE/PAA than with PVA/TMM/PAA. Further, uncured PVA/PAE/PAA was as effective as oven aged PVA/TMM/PAA in most cases.

The effect of relative humidity on the moisture content of handsheets containing PVA/TMM and PVA/PAE is presented in Fig. 45 and 46, respectively. While the results show somewhat more scatter than was encountered in the CMC/PAE series, the conclusion is the same, i.e., the presence of the additives did not reduce moisture content and, hence, the higher strength properties cannot be attributed to a difference in sheet moisture.

On the basis of the results obtained with PVA/TMM/PAA and PVA/PAE/PAA, the decision was made to abandon further work with the PVA/TMM system in favor of PVA/PAE/PAA bearing in mind that the 1% addition of polyacrylic acid was arbitrary. The fact that substantial improvements in strength were imparted by 0.5% of PAE + 1% of PAA (set 58 in Table 9) suggested that these may be the key components in this system. Nevertheless, since higher strength properties were obtained in the presence of PVA, work with a third polymer component was continued but at a reduced level of polyacrylic acid. In this direction, PVA, guar gum, and unmodified cornstarch were tested as the third polymer at a PAA addition of 0.1% b.o.f. (Guar gum and starch are known to be effective wet end adhesives and starch offers a definite price advantage over PVA and guar.) Results for this series are listed in Table 10. (Note that fresh controls are included in Table 10.) The results confirm the effectiveness of the PAE/PAA combination (Set 61) and indicate that the third polymer is not needed to attain high strength levels in the unbleached kraft pulp used in this program. However, if slightly higher moist and wet tensile factors are desired, starch would be effective at lowest cost.

Results in Table 11 and Fig. 47-51 indicate that the amount of polyacrylic acid used in combination with 0.5% of PAE has an inconsistent effect on strength properties. With one exception, optimum properties occurred at PAA additions of 0.05 - 0.2% or PAA/PAE ratios of 0.1 to 0.4. Hence, it would appear that the amount of PAA to use in combination with PAE would depend upon the properties desired. However, the 1% addition, as used in previous series, apparently represents an excess due possibly to an excess of anionic charge, whereby retention of critical components was reduced. Strength properties vs. PAA molecular weight relationships (Fig. 52-56) show a rather modest dependency on molecular weight with little or no advantage beyond a molecular weight of 104,000. This applies to moist and wet breaking length, moist Et, and dry stretch. Dry and moist TEA show a slightly greater dependency on molecular weight.

As previously indicated, the ESCA and mass spectrometer results in Table 12 were not helpful in elucidating the mechanism of strength improvement in the presence of the more effective chemical additives. It is interesting to note that a higher PAE content was found at the surface of cellophane when combined with PAA than with CMC. This may suggest greater surface reactivity for PAE/PAA, or it may merely reflect differences in surface retention.

Results in Tables 13 and 14 represent the best effort to identify, at least in part, the bonding mechanism in the treated papers. Mention should be made that the differences in the values listed in Table 14 for 1% PAE are probably not meaningful, since the method was at or near the limits of resolution. Nevertheless, the other results indicate that ester formation and covalent bonding occurred to some extent in the absence of cellulose and probably to a greater extent in the presence of fiber. These results apply only to ester formation.

Covalent bonding in the form of linkages other than esters may also be present but were not be identified in this analysis. Of course, hydrogen bonding is assumed to be present and some ionic bonding may also exist in these complex systems. The important point is that covalent bonding has been indicated to exist in the two systems which provided the highest levels of dry, moist and wet strength.

At this point it would be beneficial to describe some physical and chemical configurations which may exist in the CMC/PAE and PAA/PAE systems. Westfelt (25) proposes the following schematics to describe homo-cross-linking and co-cross-linking with cellulose fibers (Fig. 57).

In the case of homo-cross-linking, added polymer cross-links with itself or other added components and thereby traps or encases cellulose fiber surface polymer molecules possibly comprising fibrils or other fiber elements. Co-crosslinking involves bonding between added polymer and the fiber surface molecules. Both of these mechanisms could provide high levels of dry and wet strength. Fig. 58 shows possible reactions between the added polymers to form esters.

Part I in Fig. 58 shows the reaction between polyacrylic acid and the azetidinium ring of the PAE polymer to form an ester. Part II in Fig. 58 shows the reaction between carboxymethyl cellulose and the azetidinium ring; again the result is an ester, a covalently bonded structure. Both of these products could provide homo-crosslinking in the presence of fiber.

Cocross-linking between fiber and additive could conceivably occur if the carboxyl groups on cellulose react with the azetidinium group of PAE which,

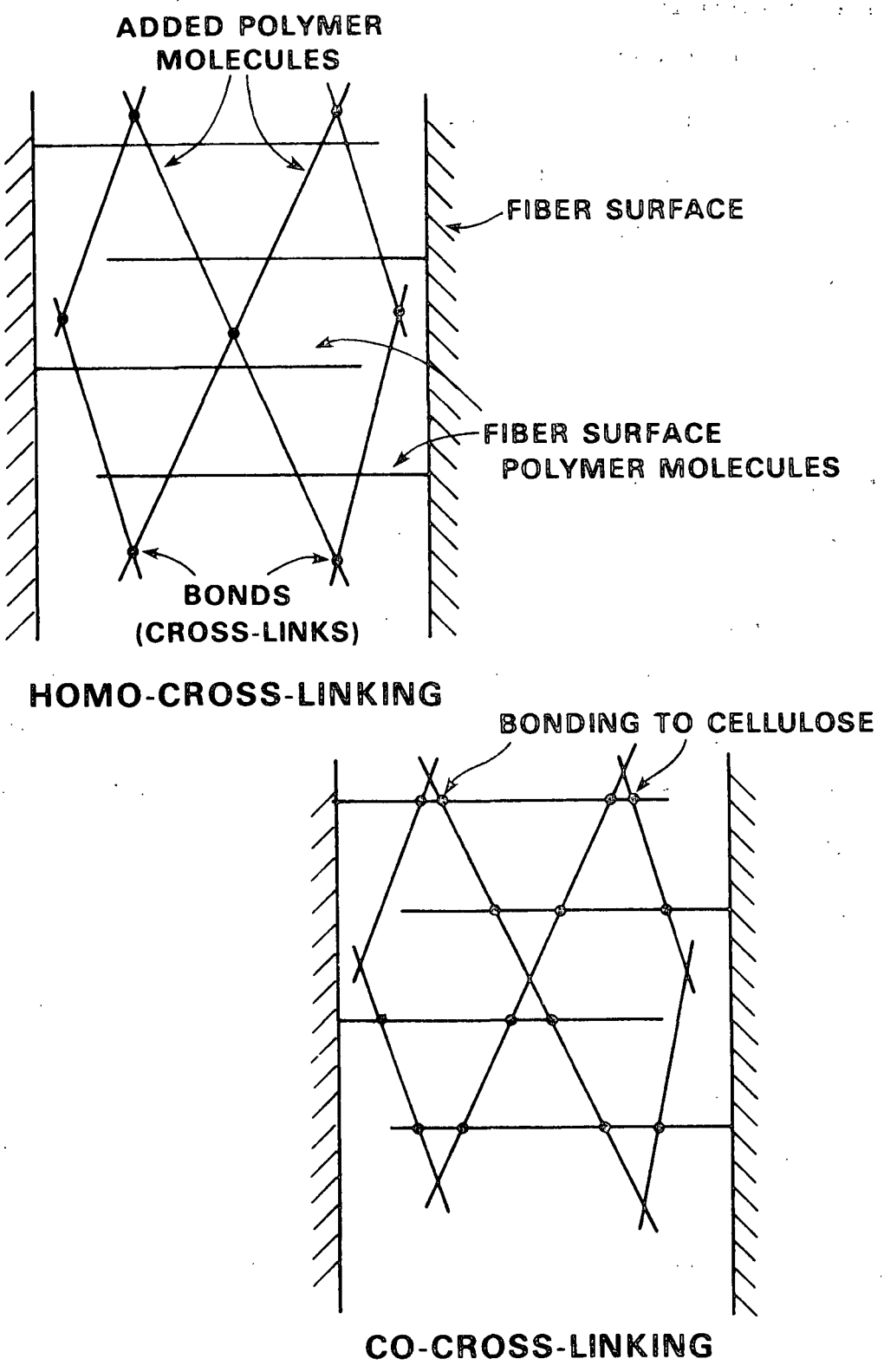
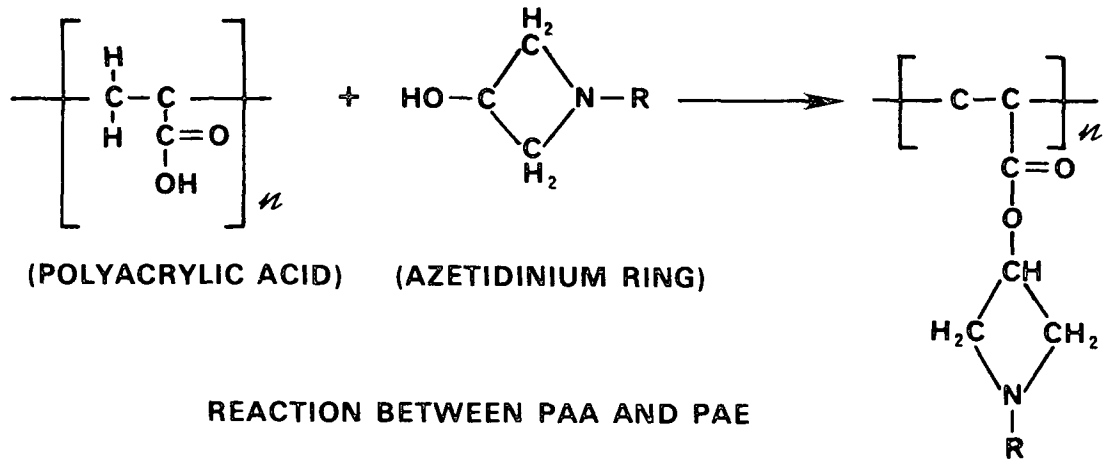


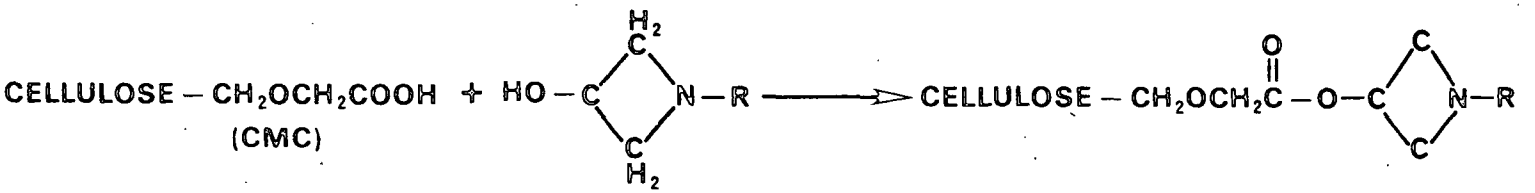
Figure 57. Bonding schematics according to Westfelt.

I



REACTION BETWEEN PAA AND PAE

II



REACTION BETWEEN CMC AND PAE

Figure 58. Reactions of added polymers to form esters.

in turn, reacts further with CMC or polyacrylic acid. Current information indicates that homo-cross-linking occurred by virtue of the results with glass fiber webs. The results with filter paper suggest that some co-cross-linking with cellulose also occurred.

The exploratory tests summarized in Table 15 indicate that papers containing the multicomponent systems can probably be repulped in about the same manner as PAE-treated papers, particularly at pH 11 and 66°C. The Thwing formation value reflects the uniformity of the paper web; the higher the number, the better the formation. The presence of undispersed fiber bundles results in poor formation and low Thwing numbers.

Presumably, extending the treatment period or increasing the temperature and pH slightly would increase the Thwing values to that of the controls, i.e., approximately 33.

In brief review, CMC/PAE and PAA/PAE combinations have been found to provide substantially improved dry, moist, and wet tensile properties compared to PAE controls in an average yield unbleached softwood kraft pulp. Other tensile properties which are important to end use in paperboard cartons stored/used under high humidity conditions were also improved. These include tensile energy absorption, extensional stiffness, and stretch. In-plane moduli and out-of-plane modulus were also improved in most cases where measured. Chemical analysis of treated papers indicates that covalent bonding occurs in these complex systems.

FUTURE WORK

Results described in this report indicate that high levels of strength can be achieved in an average yield unbleached softwood kraft pulp through the use of additive combinations which are capable of forming covalent bonds by crosslinking with themselves or with cellulose. The possibility exists that such combinations will be effective in high-yield pulps particularly if homo-cross-linking is the primary mechanism in strength enhancement. In other words, this mechanism of bonding should be effective in cases where co-cross-linking maybe inhibited by the presence of lignin residues. Accordingly, future work will examine the use of additive combinations such as CMC/PAE and PAA/PAE in pulps ranging in yield from 57-90%. The role of fines will be examined in these systems, and consideration will be given to new approaches for enhancing strength properties.

ACKNOWLEDGEMENTS

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